



Knowledge Gaps in the Cometary Spectra of Oxygen-bearing Molecular Cations

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Abstract

Molecular cations are present in various astronomical environments, most notably in cometary atmospheres and tails where sunlight produces exceptionally bright near-UV to visible transitions. Such cations typically have longer-wavelength and brighter electronic emission than their corresponding neutrals. A robust understanding of their near-UV to visible properties would allow these cations to be used as tools for probing the local plasma environments or as tracers of neutral gas in cometary environments. However, full spectral models are not possible for characterization of small, oxygen-containing molecular cations given the body of molecular data currently available. The five simplest such species (H_2O^+ , CO_2^+ , CO^+ , OH^+ , and O_2^+) are well characterized in some spectral regions but are lacking robust reference data in others. Such knowledge gaps hinder fully quantitative models of cometary spectra, specifically hindering accurate estimates of physical-chemical processes originating with the most common molecules in comets. Herein, the existing spectral data are collected for these molecules, and the places where future work is needed are highlighted, specifically where the lack of such data would greatly enhance the understanding of cometary evolution.

Unified Astronomy Thesaurus concepts: [Molecular spectroscopy \(2095\)](#); [Catalogs \(205\)](#); [Surveys \(1671\)](#); [Comets \(280\)](#)

1. Introduction

Ongoing improvements in detection limits and spectroscopic resolution in various wavelength regions have led to the discovery of many molecular and atomic emission lines in myriad astrophysical environments (McGuire 2018), not the least of which are comets (Feldman et al. 2004; Bockelée-Morvan & Biver 2017). However, there are still thousands of unidentified cometary lines from the near-UV to visible, with many likely resulting from unknown transitions of known molecules that cloud spectral classification (Brown et al. 1996; Morrison et al. 1997; Wyckoff et al. 1999; Mumma et al. 2001; Cochran & Cochran 2002; Kawakita & Watanabe 2002; Cremonese et al. 2007; Dello Russo et al. 2013; Opitom et al. 2019). Small molecular ions, such as H_2O^+ , CO_2^+ , CO^+ , OH^+ , and O_2^+ , have been observed in a variety of various astronomical environments, including comet comae and tails, planetary atmospheres, planetary disks, and the interstellar medium (ISM; Larsson et al. 2012). They are often sentinel species for underlying photochemical processes that are driven in our solar system by the Sun. Molecular radical cations also typically produce emission features at longer wavelengths than those observed from closed-shell, neutral molecules (often in the visible, whereas neutrals are in the UV). Accurate and complete spectra, if publicly available, could be used to determine if currently unidentified lines observed in cometary spectra are due to molecular cations, as exemplified by the successful attribution of previously unidentified spectral lines in comets Hyakutake and Ikeya-Zhang (Wyckoff et al. 1999; Kawakita & Watanabe 2002) to transitions from higher-excited levels of H_2O^+ (Bodewits et al. 2016). Such a database would also provide a means of quantifying the molecular cations such that ionization rates, sublimation and mass-loss rates, local plasma conditions, and potentially even cometary chemical classifications would be enhanced (Raghuram et al. 2021). To derive column densities and chemical abundances, heliocentric

velocity-dependent fluorescence efficiencies of H_2O^+ , CO_2^+ , CO^+ , and OH^+ are needed. While such values are known in part for some of these molecules, the full set of fluorescence data are lacking in many, most notably in H_2O^+ , and these knowledge gaps should be filled.

The remote identification of ions, especially in comets, requires knowledge of their spectra. The analysis and interpretation of ion data requires spectral models based on well-characterized values for dipole moments, line positions, Einstein A and B coefficients, and fluorescence efficiency factors. Surprisingly, this information is not readily available. Spectral data for these molecules are mostly missing from major databases, such as the Cologne Database for Molecular Spectroscopy (CDMS; Müller et al. 2001), the high-resolution transmission molecular absorption database (HITRAN; Gordon et al. 2017), the Virtual Planetary Laboratory (VPL) Molecular Spectroscopic Database,⁴ and the Diatomic and Triatomic spectral databases at NIST (Lovas et al. 2003, 2005). Most of these databases are predominantly geared toward applications in the IR and microwave regions, and near-UV to visible rovibronic spectra are not as well characterized. As a consequence, many currently unidentified lines can likely be attributed to these and other ions, as is the case in comet spectra (Wyckoff et al. 1999; Kawakita & Watanabe 2002; Bodewits et al. 2019), but these lines go unattributed due to a lack of the mentioned reference data.

The current hindrance of comet studies due to the lack of spectral data will be illustrated with three examples.

First, the near-UV to visible spectrum of the unusual comet C/2016 R2 (PanSTARRS) was mostly dominated by CO^+ emission, with barely any evidence of water or its fragments (McKay et al. 2019; Opitom et al. 2019; Venkataramani et al. 2020). Comparison with detailed spectral models would allow observers to carefully remove the emission of CO^+ , which

⁴ <http://vpl.astro.washington.edu/spectra/fundamentals.htm>

Table 1

Summary of the Main Emission Features of Small Molecular Cations Applicable to Rovibronic Modeling of Comet Spectra with Recommended References

Species	Transition/System	Name	Wavelength	References
H ₂ O ⁺	$A\ ^2A_1 \rightarrow X\ ^2B_1$		4200–7500 Å	Lew & Heiber (1973); Lew (1976)
H ₂ O ⁺	$B\ ^2B_2 \rightarrow X\ ^2B_1$		2200–2800 Å	Reutt et al. (1986)
H ₂ O ⁺	$B\ ^2B_2 \rightarrow A\ ^2A_1$		3000–4300 Å	Reutt et al. (1986)
CO ₂ ⁺	$A\ ^2\Pi_u \rightarrow X\ ^2\Pi_g$	Fox–Duffendack–Barker	2800–5000 Å	Fox et al. (1927); Gauyacq et al. (1975)
CO ₂ ⁺	$B\ ^2\Sigma_u \rightarrow X\ ^2\Pi_g$		2890 Å	Gauyacq et al. (1975)
CO ₂ ⁺	$C\ ^2\Sigma_g \rightarrow X\ ^2\Pi_g$		2215 Å	Wang et al. (1988); Wyttenbach et al. (1989)
CO ⁺	$B\ ^2\Sigma^+ \rightarrow X\ ^2\Sigma^+$	First Negative	2100–2500 Å	Judge & Lee (1972); Lee et al. (1974)
CO ⁺	$B\ ^2\Sigma \rightarrow A\ ^2\Pi$	Baldet–Johnson	3620–6165 Å	Dotchin & Chupp (1973)
CO ⁺	$A\ ^2\Pi \rightarrow X\ ^2\Sigma^+$	Comet Tail	4000–6000 Å	Judge & Lee (1972)
OH ⁺	$A\ ^3\Pi \rightarrow X\ ^3\Sigma^-$		3300–3600 Å	Hodges & Bernath (2017)
O ₂ ⁺	$A\ ^2\Pi_u \rightarrow X\ ^2\Pi_g$	Second Negative	1800–5300 Å	Terrell et al. (2004)
O ₂ ⁺	$b\ ^4\Sigma_g^- \rightarrow a\ ^4\Pi_u$	First Negative	4500–8500 Å	Terrell et al. (2004); Glinski et al. (2004)

Note. Where applicable, we follow the bent notation for the vibronic structure (see Cochran & Cochran 2002).

obscures the possible emission of other species (Venkataramani et al. 2020). Cochran & McKay (2018) obtained robust spectra of CO⁺ in the tail of comet C/2016 R2 (Pan-STARRS) when it was more than 3 au from the Sun, and these observations also yielded a rare, unequivocal cometary detection of N₂⁺. Prior to this result, most spectroscopic detections of N₂⁺ in comet spectra were thought to be telluric lines. The N₂⁺/CO⁺ ratio often serves as a substitute for the N₂/CO ratio in comets. The N₂/CO abundance ratio may reflect how cometary ices formed (Rubin et al. 2015). Other species may also be masked under similar circumstances, and more data are needed to feed the models for comparison.

Second, one of the most surprising results of the Rosetta mission to comet 67P/Churyumov–Gerasimenko was the detection of high amounts of O₂ in its coma (up to 10%), which has a pronounced impact on planet formation models (Bieler et al. 2015; Keeney et al. 2017). Molecular oxygen has no dipole moment and thus produces no emission from its rotational transitions. Its near-UV to visible emission features are dipole forbidden and likely weak if present (Glinski et al. 2004). On the other hand, its cation, which has been studied only at low resolution for its electronic emission as discussed later, has several emission lines in the visible regime (Table 1) that are currently lacking in full calibration. Reliable spectral models would allow observers to search for the remote emission of O₂⁺ in comets and other small bodies.

Third, CO₂ is one of the main volatiles in comets (Bockelée-Morvan & Biver 2017), and its abundance relative to H₂O and CO may link comets to their formation regions (A’Hearn et al. 2012). Unfortunately, the emission of CO₂ is blocked by the Earth’s atmosphere. However, CO₂⁺ produces bright lines in the near-UV ($B \rightarrow X$), and has been observed in many comets (see Weaver et al. 1981), as well as the less frequently observed $A \rightarrow X$ transition at longer wavelengths (Opitom et al. 2019). Observers interested in characterizing the activity and volatile content of comets would benefit greatly from digitized, electronically available high-resolution spectra along with accurate fluorescence rates that are currently not available, largely due to a lack of high-resolution experimental or theoretical results.

This paper presents a critical analysis for the state of spectroscopic data currently available (Table 1), as well as existing data gaps, for diatomic and triatomic oxygen-bearing cations that are abundant in comets: H₂O⁺, CO₂⁺, CO⁺, OH⁺, and O₂⁺. These five cations are produced by photodissociation

or electron impact of the most common cometary neutral species: H₂O, CO₂, and CO (Bockelée-Morvan & Biver 2017; Beth et al. 2020). Our discussion is limited to transitions above 200 nm, roughly the lower limit for the quantum efficiency of most CCD detectors requiring different hardware for observation. These knowledge gaps exist due to various factors ranging from difficulty of the experiments to simply a lack of motivation to study these systems. In any case, the following section describes what is currently known and offers a call to determine the remaining factors in order to produce much more insightful spectral models of comets or any other astrophysical objects where these molecules may be found.

2. Review of Existing Spectroscopic Models

2.1. H₂O⁺

The water cation first made its presence felt in planetary science in 1974 when the $A\ ^2A_1 \rightarrow X\ ^2B_1$ emission was tentatively observed nearly simultaneously by two groups (Benvenuti & Wurm 1974; Herzberg & Lew 1974) at near-UV to visible wavelengths in the tail of comet Kohoutek (1973f or C/1973 E1). Additionally, Wehinger & Wyckoff (1974) made a detection of the same transition in the tail of comet Bradfield (1974b=C/1974 C1) shortly thereafter, and follow-up work confirmed the presence of H₂O⁺ in Kohoutek (Wehinger et al. 1974), opening the door for observations in other comets. Thirteen other comets showed spectral signatures of H₂O⁺ within the next few years (Miller 1980). The high-resolution spectral atlas by Cochran & Cochran (2002) contains an inventory of 129 observed lines of three vibrational transitions of H₂O⁺ spanning the wavelength range of 5800–7500 Å in comet 122P/De Vico. Bodewits et al. (2019) used electron impact-induced spectra to attribute numerous unidentified lines in the ion tail of comet Hyakutake, reported by Wyckoff et al. (1999) and Kawakita & Watanabe (2002), to transitions from higher vibrational levels of the H₂O⁺ $A\ ^2A_1 \rightarrow X\ ^2B_1$ transition. Additionally, Lutz (1987) calculated fluorescence efficiency factors and absorption oscillator strengths for the same transition of H₂O⁺ in order to determine its abundance in the tail of comet Kohoutek.

Even with this relatively early detection of H₂O⁺ in comets, it was not until 2010 before H₂O⁺ was observed in the ISM via radiotelescopic detection toward various star-forming regions (Ossenkopf et al. 2010), and H₂O⁺ has now even been observed in older, extragalactic objects with $Z > 0.8$ with

Table 2
H₂O⁺ Vibrational Frequencies (cm⁻¹) and Rotational Constants (MHz)

State		$\nu = 0$	$\nu_1 = 1 (a_1)$	$\nu_2 = 1 (a_1)$	$\nu_3 = 1 (b_2)$
$X^2B_1^a$	$h\nu$	0.0	1408.4131	3212.8567	3259.0341
	A	870,580.8	1,001,285	851,254	835,041
	B	372,365.4	374,077.4	365,511.7	367,803.7
	C	253,880.4	249,275.7	248,680.5	349,733.7
	Δ_K	1375.3	2902.6	1348.5	1269.2
	Δ_{NK}	-155.30	-246.4	-154.6	-158.6
	Δ_N	29.66	31.00	29.80	30.23
$A^2A_1^b$	$h\nu$	13409.3	3547	876.8	
$B^2B_2^b$	$h\nu$	36757	2968	1596	

Notes.

^a All rovibrational data for the X^2B_1 state are from Muller et al. (2016), which further includes δ , Φ , ϕ , L , and ϵ values.

^b The vibronic fundamentals are compiled from Lew (1976), Reutt et al. (1986), and Jacox (2003). See text for discussion.

ALMA (Muller et al. 2016). In fact, this work exploring spectral features at such high redshift found that the existing rotational spectral data for X^2B_1 H₂O⁺ at the time were not of sufficient quality for more detailed modeling to be performed (Muller et al. 2016). The lines in the CDMS (Müller et al. 2001) matched the observations adequately in order to claim a detection, but the new rest frequencies reported in CDMS are actually those from ALMA observations combined with laboratory work done as a part of the Muller et al. (2016) study. These are listed in Table 2 for the X^2B_1 $\nu = 0$ state. Consequently, the pure rotational frequencies and spectroscopic constants of H₂O⁺ are established to high precision.

The three fundamental vibrational frequencies for X^2B_1 of H₂O⁺ in the gas phase have been determined through photoelectron and laser difference spectroscopy at 3212.86, 1408.42, and 3259.04 cm⁻¹ (Reutt et al. 1986; Jacox 2003), as shown in Table 2. Refinements to these values were made by Muller et al. (2016), extending the number of significant figures. Additionally, this refinement also generated rovibrational spectroscopic constants for these singly excited/one quantum fundamental vibrational frequencies (Muller et al. 2016), allowing for accurate rovibrational models of H₂O⁺ to be produced. However, the electronic and vibronic bands are still incomplete.

The electronic spectral characterization of H₂O⁺ coincided with its initial observation in comet Kohoutek. Work by Lew & Heiber (1973) and Lew (1976) provides clear descriptions of the electronic feature for the $A^2A_1 \rightarrow X^2B_1$ transition, but the full vibronic nature of any excited state has yet to be established. The A^2A_1 and B^2B_2 states have accurate transition energies from photoelectron experiments (Reutt et al. 1986), putting the $B^2B_2 \rightarrow X^2B_1$ transition in the 2200–2800 Å range, and the $B^2B_2 \rightarrow A^2A_1$ transition in the 3000–4300 Å range, as given in Table 1. These ranges, while largely estimated for the two transitions involving the B^2B_2 state, are well separated, giving H₂O⁺ full emission coverage from 2200 Å through the UV to the very edge of the visible regime at 7500 Å. More resolved electronic transition wavelengths to at least the subnanometer scale, and certainly more accurate and complete vibrational levels to at least the single cm⁻¹ scale for these electronically excited states of H₂O⁺, are needed in order to model these spectra more effectively. Additionally, more narrowly defined state lifetimes (and hence, Einstein coefficients) are needed because the current

measurements are more than 40 yr old and two different studies disagree with one another by nearly a factor of three (Curtis & Erman 1977; Möhlmann et al. 1978).

The experimental photoelectron results given in Table 2 only produce estimates for fundamental vibrational frequencies, and only for the a_1 modes (Reutt et al. 1986). The ν_2 bend of the A^2A_1 state at 876.8 cm⁻¹ is the most concretely established fundamental frequency based on comparisons between the photoelectron data and the prior existing emission spectra (Lew 1976; Reutt et al. 1986; Jacox 2003). These values guided electron impact studies that established many of the experimental rovibronic bands for the ν_2 bend of the A^2A_1 state (Kuchenev & Smirnov 1996). Subsequent quantum chemical vibronic lines in the $A^2A_1 \rightarrow X^2B_1$ transition were compared to those from the electron impact study. The error is less than 2 cm⁻¹ for this purely theoretical study (Wu et al. 2004), providing high-accuracy vibronic lines for higher quanta of the A^2A_1 ν_2 bend. These, in turn, were subsequently corroborated and extended experimentally (Gan et al. 2004). Even so, no lines or spectroscopic constants for higher quanta in either of the other two modes of A^2A_1 , or for any modes of the B^2B_2 state, are currently given in the literature. Noble gas tagging experiments have produced estimates for the hydride stretches, but the proton-bound nature of these complexes likely makes them irrelevant with regard to the reference data required of H₂O⁺ (Dopfer et al. 2001; Roth et al. 2001).

Consequently, the high-accuracy spectral data (both experimental and theoretical) available for the water cation from the literature currently consist of:

1. Pure rotational spectroscopic constants and lines available in CDMS;
2. Fundamental vibrational frequencies and rovibrational spectroscopic constants that can be produced from Muller et al. (2016);
3. Onset energies for the $A^2A_1 \rightarrow X^2B_1$, $B^2B_2 \rightarrow X^2B_1$, and $B^2B_2 \rightarrow A^2A_1$ transitions (Lew & Heiber 1973; Lew 1976; Reutt et al. 1986; Jacox 2003);
4. The ν_2 bands of the A^2A_1 state provided by Wu et al. (2004).

The remaining data necessary for proper cometary or other astrochemical modeling are the rovibrational spectroscopic constants and lines for the A^2A_1 and B^2B_2 excited states, save for the ν_2 bands of the A^2A_1 state as established by Kuchenev & Smirnov (1996), Wu et al. (2004), and Gan et al. (2004). These electronic states lie at 7457.7 Å and 2708.7 Å above the ground state (Lew & Heiber 1973; Lew 1976; Reutt et al. 1986; Jacox 2003), making them the only two states of interest for purely solar excitation models like those for comets. Hence, full modeling of H₂O⁺ in comets will require line lists for these two electronic states, which are currently unavailable from any previous experimental or theoretical studies. Finally, Einstein coefficients for transitions involving each of these states are also needed in order for the spectral models to be complete.

2.2. CO₂⁺

The detection of the carbon dioxide cation predates that of H₂O⁺ by nearly 25 yr. Observations of the long-period comet Bester (1947k or C/1947 F1) acquired as it was approaching the Sun revealed numerous bands of the CO₂⁺ $\tilde{A}^2\Pi_u \rightarrow \tilde{X}^2\Pi_g$ emission transition in the comet tail at wavelengths from 3500 to 5000 Å (Swings & Page 1950). The spectrum of this

Table 3
CO₂⁺ Vibrational Frequencies (cm⁻¹) and Rotational Constants (MHz)

State		$\nu = 0$	$\nu_1 = 1 (\sigma_g^+)$	$\nu_2 = 1 (\pi_g)$	$\nu_3 = 1 (\sigma_u^+)$
$X \ ^2\Pi_g^a$	$h\nu$	0.0	1264.98	513.262	1423.08
	B	11,410		11 380	
	D	0.033			
$A \ ^2\Pi_u^a$	$h\nu$	28,500.35	1122.41	466.75	2653.07
	B	10 500			
$B \ ^2\Sigma_u^{+b}$	$h\nu$	34,591.6	1284	590	1891
	B	11 340		11 500	
	D	0.069			
$C \ ^2\Sigma_g^{+c}$	$h\nu$	45,157	1384	614	1567
	B	11 837	11 820		
	D	0.1	0.1		

Notes.

^a Data collected from Gauyacq et al. (1975), Varfalzy et al. (2007), Gharaibeh & Clouthier (2010), and Jacox (2003).

^b Data collected from Gauyacq et al. (1975) and Jacox (2003).

^c Data collected from Wang et al. (1988), Wyttenbach et al. (1989), and Jacox (2003).

molecule had been known since the late 1920s (Fox et al. 1927; Duffendack & Smith 1929) and was refined in the early 1940s (Mrozowski 1941), but comet Bester provided the first natural observation of CO₂⁺ beyond the Earth’s atmosphere. Both CO₂⁺ $\tilde{A} \ ^2\Pi_u \rightarrow \tilde{X} \ ^2\Pi_g$ and the $\tilde{B} \ ^2\Sigma_u^+ \rightarrow \tilde{X} \ ^2\Pi_g$ transitions were observed by Mariner 6 and Mariner 7 in the dayglow of Mars (Barth et al. 1971). Sounding rocket observations of comet C/1975 V1 (West) yielded the first cometary detection of the CO₂⁺ $\tilde{B} \ ^2\Sigma_u^+ \rightarrow \tilde{X} \ ^2\Pi_g$ transition in the near-UV (Feldman & Brune 1976). The detection of CO₂⁺ also predates the first cometary observation of the neutral by 36 yr, when its fluorescence spectrum was observed by the Vega 1 probe to comet 1P/Halley in 1986 (Combes et al. 1986). Later, the emission of neutral CO₂ was first discovered in the ISM via IR spectra in 1989 via the bright antisymmetric stretch mode (d’Hendecourt & Jourdain de Muizon 1989), but the cation has yet to be documented in any environment beyond the solar system.

The vibronic spectrum of CO₂⁺ is very well established, albeit very complicated (Gauyacq et al. 1975). This molecular spectrum is known primarily due to its presence in comet Halley (Johnson & Rostas 1995). As referenced in Table 3, high-precision experimental results are available for the ground state ($X \ ^2\Pi_g$) and first excited state ($A \ ^2\Pi_u$ at 3508.73 Å), along with detailed, though less precise, data for the higher $B \ ^2\Sigma_u^+$ (2890.88 Å) and $C \ ^2\Sigma_g^+$ (2214.88 Å) states (McCallum & Nicholls 1972; Frye & Sears 1987; Wang et al. 1988; Wyttenbach et al. 1989; Chambaud et al. 1992; Johnson & Rostas 1995; Liu et al. 2000; Jacox 2003; Lovas et al. 2003; Shaw & Holland 2005; Gharaibeh & Clouthier 2010). These higher states, especially the $C \ ^2\Sigma_g^+$, also lie beyond what can be excited through photofluorescence, the dominant emission mechanism for most cometary fragment species (Shaw & Holland 2005). Johnson & Rostas (1995) provide a thorough review of the state of CO₂⁺ spectral data that were available at the time of their publication. This molecule has problematic Fermi resonances, Renner–Teller distortions, and vibronic couplings (Varfalzy et al. 2007), all of which shift the spectral

lines from the locations predicted by the standard model and put vibrational transitions of electronically excited states in competition with other features, making them difficult to clearly delineate.

However, Chambaud et al. (1992) report an extensive, experimentally benchmarked list of theoretically computed vibronic transitions within 5000 cm⁻¹ of the $X \ ^2\Pi_g$ ground state for CO₂⁺, where the complicated interactions are mitigated through control of the quantum chemical computations employed. These values have been corroborated and extended more recently by Liu et al. (2000) and Gharaibeh & Clouthier (2010), among others, through pulsed field ionization as well as photoelectron- and laser-induced fluorescence, respectively, to more than 10,000 cm⁻¹ beyond the onset of the $A \ ^2\Pi_u$ state. Rotational and spectroscopic constants have also been provided for the fundamental frequencies of the IR-allowed ν_3 mode of the ground electronic state, as well as the ν_1 and ν_3 modes of the $A \ ^2\Pi_u$ state via high-precision emission spectroscopy (Johnson & Rostas 1995). Similar to its neutral counterpart, CO₂⁺ does possess the bright ν_3 antisymmetric stretching mode, but the intensity of this mode for the cation is reduced by approximately 75% compared to its neutral counterpart, according to double-harmonic quantum chemical computations performed presently.

Photofluorescence efficiencies for the most important bands in the $A \ ^2\Pi_u \rightarrow X \ ^2\Pi_g$ and $B \ ^2\Sigma_u^+ \rightarrow X \ ^2\Pi_g$ transitions have been determined by Kim (1999), using the transition probability data of McCallum & Nicholls (1971), and the results were compared to ground-based spectra of comets Austin (1989c1=C/1989 X1) and 21P/Giacobini–Zinner. Kim (1999) argued that the Swings effect did not significantly affect the fluorescence efficiency of the CO₂⁺ transitions and that the accuracy of their model was mostly limited by spectroscopic data (line positions and transition probabilities) available to them. Furthermore, their equilibrium model only includes vibrational–vibrational transitions, unlike the aforementioned studies in the prior paragraph and others (Itikawa et al. 2001), which cover rovibrational transitions and focus heavily on the Renner–Teller effect. However, as demonstrated in the discussion above, significant work has been done to understand the spectrum of CO₂⁺ after their study was published, thus meriting a re-evaluation of the data. Consequently, a majority of the necessary spectral data to model CO₂⁺ should already be available from these references, which are largely curated at NIST (Lovas et al. 2003). The exceptions are the vibrationally excited rotational constants of the excited electronic states and absolute line intensities (oscillator strengths) for these transitions, as most of the currently available ones are relative at best. While not as necessary for the production of the electronic band progressions, having the full rovibronic scope of data, Einstein coefficients, and the absolute intensities would produce the most accurate and descriptive models for comparison to observation.

The $C \ ^2\Sigma_g^+$ state has not been observed in comets even though excitations into the longer wavelength $B \ ^2\Sigma_u^+$ state have been observed from space-based instruments (Weaver et al. 1981). However, some rovibrational data for this state are known with fairly high resolution (Wyttenbach et al. 1989), especially the excitation energy and the rotational constants. However, the rotational quartic distortion D constant was held fixed in the work by Wyttenbach et al. (1989) for each vibrational state. Wang et al. (1988) and Wyttenbach et al. (1989) disagree as to

the assignment of the ν_1 symmetric stretching frequency (1352 cm^{-1} versus 1384 cm^{-1} , respectively), but the latter also reports the B rotational constant for this mode, lending more credence to their assignment. The other fundamental vibrational frequencies are from Wang et al. (1988), and the rotational data for these modes are also missing. Hence, the $C\ ^2\Sigma_g^+$ state of CO_2^+ could also benefit from more advanced study. Such data may be able to isolate this state in cometary spectra in regions that are difficult to observe. Such observations, however, can only occur if more data are on hand for fluorescence models to compare with observation.

Transitions between the various excited electronic states of CO_2^+ are also possibly originating from solar radiation. However, most are at near-infrared wavelengths and would likely have relatively low molecular state populations involved in such transitions, giving little signal. Additionally, such weak signals also create challenges for producing high-resolution experimental spectral data in the laboratory. Regardless, the $B\ ^2\Sigma_u^+ \rightarrow A\ ^2\Pi_u$ transition should take place at $16417\text{ \AA}$, based on the difference in the electronic energies for each of these states from Gharaibeh & Clouthier (2010) and Johnson & Rostas (1995). The $C\ ^2\Sigma_g^+ \rightarrow A\ ^2\Pi_u$ transition wavelength is actually in the visible region at $6003.6\text{ \AA}$ (Wytenbach et al. 1989), leaving the $C\ ^2\Sigma_g^+ \rightarrow B\ ^2\Sigma_u^+$ in between these two at $9464.9\text{ \AA}$. The photofluorescence models of CO_2^+ would also benefit from data for these excited states even if they would be minor contributors to the overall cometary spectra of interest.

2.3. CO^+

The detection of the $A\ ^2\Pi_i \rightarrow X\ ^2\Sigma^+$ transition of CO^+ at $4820\text{ \AA}$ represents the earliest cometary detection of the cations discussed here (Swings 1965). The spectra of the tails from comet C/1907 L2 (Daniel) and the exceptionally bright comet C/1908 R1 (Morehouse) both yielded correspondence to emission bands that were soon matched to discharge spectra acquired in the laboratory (Fowler 1909). Owing to the low sublimation temperature of CO, CO^+ emission can be seen in comet spectra at distances exceeding 5 au (Cochran & Cochran 1991). CO^+ has subsequently been utilized as a spectral reference point in the cometary detection of CO_2^+ and OH^+ (Swings & Page 1950).

Extrasolar rotational lines of CO^+ were first observed toward the photodissociation region M17SW in 1993 (Latter et al. 1993), further showcasing the near-century lag between comet cation chemistry and interstellar cation chemistry. CO^+ has since been observed toward other photodissociation regions, planetary nebulae, in the disk of M82, and in the circumnuclear torus of Cygnus-A (Fuente et al. 2000, 2006; Bell et al. 2007; Stäuber & Bruderer 2009). Even though CO^+ had been known in comets previously from near-UV to visible spectra, the established $J = 2 \rightarrow J = 1$ rotational line of CO^+ was also observed in comet Hale-Bopp with the Caltech Submillimeter Observatory in 1997 (Lis et al. 1997a, 1997b). However, more modern spectral benchmark data would greatly enhance the spectral resolution needed to inform more detailed future observations.

There is an extensive body of work reporting on spectral data of CO^+ that has spanned multiple decades with most of the modern foundation coming the past 40 yr (Marchand et al. 1969; Brown et al. 1984; Kuo et al. 1986; Haridass et al. 1992; Bembenek et al. 1994). The current state of knowledge is listed

Table 4
 CO^+ Vibrational Frequencies (cm^{-1}) and Rotational Constants (MHz)^a

State		$\nu = 0$	$\nu = 1$
$X\ ^2\Sigma^+$	$h\nu$	0.0	2183.9
	B	59,270.5	
	D	0.190	
$A\ ^2\Pi$	$h\nu$	20,733.3	1534.9
	B	47,649	
	D	0.20	
$B\ ^2\Sigma^+$	$h\nu$	45,876.7	1678.3
	B	53,930	
	D	0.23	

Note.

^a Data collected from Irikura (2007) and Hakalla et al. (2019).

in Table 4. Some of the most complete examinations for the spectral classification of CO^+ are from observations of cometary ion tails (Vujisić & Pesić 1988; Haridass et al. 2000; Kepa et al. 2004) and from quantum chemical explorations (Lavendy et al. 1993; Xing et al. 2018). A very recent laboratory-based Fourier-transform emission spectral examination of this simple molecule has revealed an extensive trove of rovibronic data for the $A\ ^2\Pi_i \rightarrow X\ ^2\Sigma^+$ transition (Hakalla et al. 2019). The experimental data are fit from previous known values, including additional reference points from the $B\ ^1\Sigma^+ \rightarrow A\ ^1\Pi$ transition of neutral carbon monoxide. In turn, these results have been used to provide input parameters for spectroscopic modeling with the PGOPHER software (Western 2017). The remaining, highly resolved ($\sim 1\text{ cm}^{-1}$) experimental lines were then matched with the output from PGOPHER such that the rest of the $A\ ^2\Pi_i \rightarrow X\ ^2\Sigma^+$ rovibronic features within 2000 cm^{-1} of the onset are classified. Hence, the data necessary to model CO^+ have been produced and are curated within this paper, but are not accessible in a standard format beyond that listed in the data tables.

Magnani & A’Hearn (1986) performed a comprehensive series of calculations on the fluorescent equilibrium of CO^+ . Unlike prior studies, they included the Baldet–Johnson bands and the first negative bands. The data used for their calculations were based on a compilation of nearly two dozen empirical and theoretical papers. Line positions (given in cm^{-1}) were taken from Schmid & Gerö (1933), Bulthuis (1934), Narahari Rao (1950a), and Herzberg (1950). Oscillator strengths were drawn from Joshi (1966) and Jain (1972). The Frank–Condon factors were taken from Nicholls (1962), and Hönl–London factors were utilized from Narahari Rao (1950b), Narahari Rao & Sarma (1953), and Schadee (1964). Transition probabilities were based on Arpigny (1976) and Crovisier (1985). Information on transitions were taken from Kopelman & Klemperer (1962), Arpigny (1964a, 1964b), Certain & Woods (1973), Feldman & Brune (1976), Rosmus & Werner (1982), and Chin & Person (1984). Lab measurement data from Lawrence (1965) and Judge & Lee (1972) were also used. Formulas for the Einstein A and B coefficients were taken from Schleicher & A’Hearn (1982). Solar spectral data for the full solar disk were taken from Broadfoot (1972) and A’Hearn et al. (1983). Because the oscillator strength for the Baldet–Johnson bands was unknown, Magnani & A’Hearn (1986) assigned a value such that transition probabilities were in agreement with

available laboratory observations, resulting in projected band intensities that were uncertain but likely still reliable at the 20% level and consistent with their nondetection in most comets. Tables are provided in their paper with the fluorescence efficiencies of 60 transitions for a range of heliocentric velocities between -50 and $+350$ km s $^{-1}$. However, as explained in our discussion above, significant work has been done on the spectrum of CO $^+$ after the Magnani & A'Hearn (1986) paper was published (see Table 4 for recommended constants and frequencies). These recent studies, such as Xing et al. (2018) and Hakalla et al. (2019), have increased the spectral resolution as well as the accuracy of known transitions. As such, the fluorescence model of CO $^+$ would benefit from including these spectral models.

2.4. OH $^+$

The A $^2\Sigma^+ - X^2\Pi$ emission of neutral OH around 3085 Å is readily used to derive water production rates of comets (see A'Hearn et al. 1995), and in the ISM, the hydroxyl radical was actually the first molecule to be observed via rotational spectroscopy in 1963 toward the very powerful radio source in the Cas A supernova remnant (Weinreb et al. 1963) and has since been observed in diffuse clouds, as well (Neufeld et al. 2010; Porras et al. 2013). Both OH $^+$ and CO $_2^+$ were observed first in comet C/1947 F1 (Bester) (Swings & Page 1950). The dominant feature for this OH $^+$ observation is what spectroscopists now label as the A $^3\Pi \rightarrow X^3\Sigma^-$ transition between 3300–3600 Å. This broad emission feature may contaminate observations acquired with comet narrowband filters designed for continuum measurements or for the emission of NH around 345 nm (Bodewits et al. 2016). Outside comets, OH $^+$ was not observed until 2010, toward Sgr B2 (Wyrowski et al. 2010) and background stars at near-UV wavelengths (Krelowski et al. 2010). OH $^+$ has also been observed around ultraluminous galaxies (van der Werf et al. 2010), toward a lensed quasar (Muller et al. 2016), in the Orion bar (van der Tak et al. 2013), and in cometary knots of planetary nebulae (Aleman et al. 2014; Priestley & Barlow 2018).

Like with CO $^+$, the foundational experimental spectroscopic work on OH $^+$ comes from the previous 40 yr or so (Merer et al. 1975; Bekooy et al. 1985; Gruebele et al. 1986; Liu et al. 1987; Rehfuß et al. 1992; Varberg et al. 1994). During this same era, Saxon & Liu (1986) conducted a theoretical study of OH $^+$ photodissociation from the ground state and calculated potential curves for each of the lowest three Σ^- and Π states. They also evaluated transition dipole moments between the ground and excited states and used them to calculate photodissociation cross sections. Gómez-Carrasco et al. (2014) conducted a theoretical study of OH $^+$ that included calculating the Einstein coefficients for rovibrational bands involving the X $^3\Sigma^-$ and A $^3\Pi$ electronic states and calculating the state-to-state rate constants for inelastic collisions between He and OH $^+$ (X $^3\Sigma^-$). A more recent study by Hodges et al. (2018) combines empirical energy surfaces with the Rydberg–Klein–Rees method, dipole moment calculations calculated quantum chemically, and oscillator strengths and Einstein A coefficients calculated using PGOPHER. Line lists are created with positions, oscillator strengths, and Einstein A coefficients for the A $^3\Pi \rightarrow X^3\Sigma^-$ rovibronic transition and the rovibrational transitions of the X $^3\Sigma^-$ ground state, including the following levels: (A, $\nu = 0, 1$; X, $\nu = 0, 1, 2, 3, 4$) up to $J'' = 30$. The line positions of the A $^3\Pi \rightarrow X^3\Sigma^-$ band (3300–3600 Å) are compared to those determined using a discharge cell combined with a Fourier transform spectrometer (Hodges & Bernath 2017).

Table 5
OH $^+$ Reported Vibrational Frequencies (cm $^{-1}$) and Rotational Constants (MHz)^a

State		$\nu = 0$	$\nu = 1$
X $^3\Sigma^-$	$h\nu$	0.0	2956.358469
	B	492,346.37	470,531.9
	D	57.6099	56.0145
	H	0.003942	0.003903
A $^3\Pi$	$h\nu$	27935.6930	1975.9872
	B	400,841.1	375,144.7
	D	68.056	65.8854
	H	0.004350	0.003007

Note.

^a Data collected from Hodges & Bernath (2017).

The authors state that there is no intensity measurement to verify the vibrational transitions (around 3.4 μ m) of the X–X band. A table of their data is available electronically through the VizieR database, and the pertinent rovibronic features of OH $^+$, are listed in Table 5.

2.5. O $_2^+$

Surprisingly, neutral molecular oxygen was detected at relatively large abundances with the ROSINA and Alice instruments on board Rosetta as it orbited comet 67P/Churyumov–Gerasimenko (Bieler et al. 2015; Keeney et al. 2017). It is unclear whether this O $_2$ was present at the comet's formation, is trapped in cometary ices or clathrates (Luspay-Kuti et al. 2018), or is produced by a chemical reaction with materials on the surface or in the coma (Fortenberry et al. 2019). Although its presence in cometary atmospheres was first suggested 70 yr ago (Swings & Page 1950), the molecular oxygen cation actually has not been detected remotely to date in either cometary or interstellar media (Glinski et al. 2004), and was only spuriously detected *in situ* by Rosetta's ROSINA instrument (Beth et al. 2020). Three faint rotational lines for the X $^3\Sigma_g^-$ system of O $_2$ were finally detected in 2011 toward Orion (Goldsmith et al. 2011), but the cation remains elusive for detection in the ISM as well as in comets. In comets, photoionization rates for the production of O $_2^+$ from O $_2$ are larger ($\sim 10\%$) than for the production of H $_2$ O $^+$ by photoionization of H $_2$ O ($\sim 3\%$; Huebner & Mukherjee 2015), implying that O $_2^+$ should be present as well, especially outside the collisionally thick inner coma where it can quickly dissipate through chemical reactions (Beth et al. 2020). However, high-quality spectral reference data and fluorescence efficiency rates are needed to look for its signature in cometary and other astrophysical spectra.

Li et al. (2000) present results of laser-induced fluorescence (LIF) of the (8,0) and (8,1) bands of the A $^2\Pi_u \rightarrow X^2\Pi_g$ system (between 1800 and 5300 Å), as well as preliminary LIF determinations of ($\nu=0, 1$) distributions from reactions involving Ar $^+$ and Xe $^+$. Electron impact ionization-induced spectra between 2200 and 6000 Å are presented in Terrell et al. (2004), and these are gathered in Table 6. They present a simplified molecular model to interpret their data, which includes A $^2\Pi_u \rightarrow X^2\Pi_g$ and b $^4\Sigma_g^- \rightarrow a^4\Pi_u$ (between 4500–8500 Å). All other excitations are outside the window of solar radiation observed from the ground (Lovas et al. 2005),

Table 6 O_2^+ Reported Vibrational Frequencies (cm^{-1}) and Rotational Constants (MHz)^a

State		$\nu = 0$	$\nu = 1$
$X^2\Pi_g$	$h\nu$	0.0	1872.27
	B	50,704	
	D	0.159	
$A^2\Pi_u$	$h\nu$	40,669.3	871.11
	B	31,829	
	D	0.178	

Note.^a Data collected from Irikura (2007).

and spin-flip excitations are not likely to produce any measurable intensity under cometary conditions. The models of these band features were made possible by the rotational constants and strong classification of the vibrational fundamental from Lovas et al. (2005). The fundamental frequency varies significantly across these four states from 898.2 cm^{-1} in $A^2\Pi_u$ (Colburn & Douglas 1977) to 1904.7 cm^{-1} in the ground $X^2\Pi_g$ state, where these bookend the 1580.19 cm^{-1} fundamental in the $X^3\Sigma_g^-$ in the neutral (Lovas et al. 2005). The rotational constants vary from 31,829 MHz to 50,704 MHz, again respective of $A^2\Pi_u$ and $X^2\Pi_g$ (Irikura 2007). Consequently, the rovibronic lines have notably different progressions within them in the doublet excitation of the shorter wavelengths.

3. Conclusions

The state of available spectral data for small, oxygen-containing molecular cations is mixed but is rife with notable knowledge gaps that hamper the full diagnostic use of the emission of molecular ions. These holes must be filled in order to better understand physical processes and chemical evolution for tenuous atmospheres of various astronomical bodies, such as comets around perihelion. General near-UV to visible spectral progressions are largely established for these molecules, and the rovibrational natures of the ground electronic states have been well classified for these relatively simple molecules. However, a rigorous, quantitatively predictive analysis of the full rovibronic structure, especially the rotational constants of the excited rovibronic states, is currently lacking in most cases. Existing excitation models are decades old, and rely on limited spectral models. This work shows where the data in these models can and should be improved.

The worst case of the current state of knowledge of the spectral properties of the H_2O^+ , CO_2^+ , CO^+ , OH^+ , and O_2^+ set is the water cation, where only low-resolution characterization for the rovibrational transitions of the two lowest electronic states is currently available in the literature. These available data are also mostly limited to the vibrational band positions and have no rotational substructure described. While surprising for a molecular product of such a common and abundant molecule, this represents a readily surmountable challenge for spectroscopic characterization for the astrochemical community for both high-resolution experiment and modern quantum chemistry, if not in a combination of the two approaches. The reference data for CO_2^+ and CO^+ have similar rotational spectral holes, but the vibronic spectra of the higher electronic states have been explored at high resolution for the most part. In any case, these small, oxygen-containing molecular cations

and their daughter species are often observed in bodies such as comets, but clear identification of the lines, especially the rovibronic features, is necessary in order to gain deeper insights into the photochemistry playing out in various solar system environments.

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