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Communication

Dibridged, Monobridged, Vinylidene-Like, and Linear Structures for the Alkaline Earth Dihydrides Be_2H_2, Mg_2H_2, Ca_2H_2, Sr_2H_2, and Ba_2H_2. Proposals for Observations

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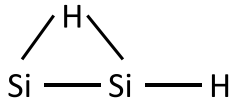
ABSTRACT: This research reports a search for peculiar monobridged structures of the E_2H_2 molecules (E = Be, Mg, Ca, Sr, Ba). For Be_2H_2 and Mg_2H_2, the monobridged geometry is not an equilibrium but rather a transition state between the vinylidene-like structure and the global minimum HE−EH linear geometry. However, for Ca_2H_2, Sr_2H_2, and Ba_2H_2, this situation changes significantly; the linear structure is no longer the global minimum but lies higher in energy than two other equilibria, the dibridged and monobridged structures. The planar dibridged structures of both Sr_2H_2 and Ba_2H_2 should be observable via IR spectroscopy. Although the remarkable monobridged structures lie 8.3 (Sr) and 7.6 kcal/mol (Ba) higher, the large IR intensities of the terminal E−H stretching frequencies may make the monobridged structures observable. The monobridged structures have sizable permanent dipole moments (3.07 and 3.06 D for Sr and Ba, respectively) and also should be observable via microwave spectroscopy.

In 1990, Colegrove and Schaefer[1] made the prediction of an unprecedented Si_2H_2 monobridged equilibrium geometry (**1**).



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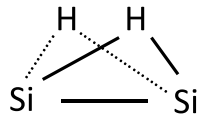
The Colegrove structure was predicted to lie only 10 kcal/mol above the earlier-predicted (Lischka, 1983)[2] ground-state butterfly structure of Si_2H_2 (**2**).



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Lischka and Köhler did not consider the Colegrove monobridged structure. With theoretical support from Grev,[3] in 1992 Codonnier and co-workers[4] reported the remarkable observation via microwave spectroscopy (148 lines) of the monobridged Si_2H_2 (**1**).

These discoveries were quickly followed by the discovery of new monobridged equilibrium geometries for Al_2H_2, Ga_2H_2, and Ge_2H_2. Later (2005), Lein and co-workers[5] reported monobridged equilibrium geometries for Sn_2H_2 and Pb_2H_2.

Our interest in these E_2H_2 structures was reignited by the experimental studies of Mukherjee and co-workers.[6] These authors reported the synthesis of a new family of alkaline-earth metal compounds, including compounds incorporating the dibridged CaH_2Ca moiety. Naturally, we were curious whether the Ca_2H_2 system could support a monobridged equilibrium geometry. It was found that there is indeed a monobridged structure, as illustrated in Figure 1. There it is seen that the dibridged structure is the global minimum but only 6.4 kcal/mol below the monobridged structure. Perhaps surprising, the unobserved monobridged structure lies 6.4 kcal/mol *below* the conventional experimentally observed linear structure HCa−CaH. Furthermore, the unobserved dibridged structure of Ca_2H_2 lies 12.8 kcal/mol *below* the linear HCa−CaH.

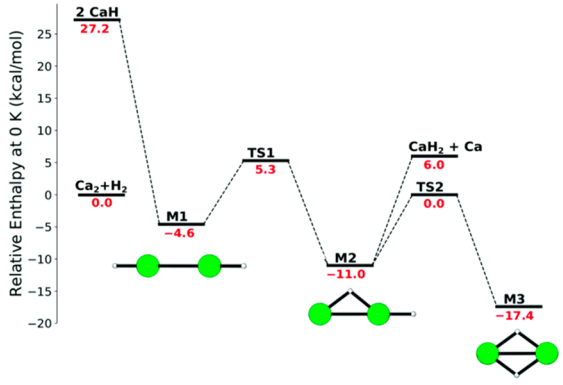

Figure 1. Features of the PES for Ca_2H_2. See ref 7.

Be_2H_2. In this Communication, we focus on four other E_2H_2 molecules, namely, those with E = Be, Mg, Sr, and Ba.

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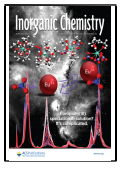

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Table 1. Relative Energies (kcal/mol) for E_2H_2 Structures

	Linear	Dibridged	Monobridged	Vinylidene	H—E—H
	H—E—E—H				E···H—E—H
Be_2H_2	0.0	+36.8	+39.4	+25.3	+25.8
Mg_2H_2	0.0	+10.5	+25.2	+4.0	+5.0
Ca_2H_2[a]	0.0	-9.0	-3.3	+7.4	+4.8
Sr_2H_2	0.0	-16.4	-8.1	+5.5	+1.7
Ba_2H_2	0.0	-19.6	-12.0	+6.1	-0.6

[a]Results were obtained at the CCSD(T)/cc-pVQZ level of theory.

The Be_2H_2 molecule was prepared in 1993 by Tague and Andrews.[8] They assigned IR features at 1901 cm^{-1} (Be_2H_2) and 1533 cm^{-1} (Be_2D_2) to the expected linear structure HBe−BeH. The most reliable theoretical study to date of Be_2H_2 is that of Lundell and Boldyrev.[9] They predicted the vinylidene-like structures H_2BeBe to lie 30 kcal/mol above the expected linear structure.

In the present study, a systematic search for the monobridged Be_2H_2 structure was carried out using the coalescence kick (CK) algorithm.[10] About 10000 trial structures were generated, followed by geometry optimizations using the density functional theory (DFT) method. The lowest-energy isomers were then reoptimized with the more reliable CCSD(T)/cc-pVQZ method. The geometries of optimized isomers could be found in Figure S1. We found that the monobridged Be_2H_2 structure is a *transition state* between the vinylidene-like and conventional linear HBe−BeH structures. The monobridged structure is predicted to lie 14.1 kcal/mol above the vinylidene-like structure, which, in turn, lies 25.3 kcal/mol above the global minimum linear HBe−BeH structure. It is clear that there is no monobridged equilibrium geometry for Be_2H_2. We also discovered a linear Be···HBeH structure, which was predicted to be 25.8 kcal/mol above the HBe−BeH global minimum. The relative energies of all species are listed in Table 1.

The chemical bonding patterns of the investigated species were analyzed using the adaptive natural density partitioning (AdNDP) algorithm, as implemented in *AdNDP 2.0* code.[11] It was shown that the vinylidene-like structure and Be···HBeH linear structure could be described in terms of classical Lewis one-center two-electron (1c−2e) lone pairs and two-center two-electron (2c−2e) bonds. Thus, in both structures, the BeH_2 fragment is present (consisting of two 2c−2e Be−H σ bonds), while the remaining Be atom binds to the rest of the structure with a van der Waals interaction. In turn, the valence electrons of the monobridged and linear HBe−BeH structures can be localized into two 2c−2e Be−H and one 2c−2e Be−Be σ bonds. The complete chemical bonding patterns could be found in Figure S1.

The electronic structure of the Be_2H_2 dibridged structure exhibits a very interesting feature. We found that four valence electrons form two 3c−2e bonds binding Be and H atoms together. The remaining two electrons are localized into two 1c−1e s-type unpaired electrons on the Be atoms (Figure 2). This result pushes us to the conclusion that the electronic structure of dibridged E_2H_2 species can be described as an unrestricted singlet. Performing the CASSCF(6e,9o)/NEVPT2 calculations,[12,13] we showed that the wave function in the singlet state indeed has a multiconfigurational character, while the triplet state is almost perfectly described by a single-determinant wave function. The same pattern was observed for all dibridged E_2H_2 structures. Despite the multiconfigurational character of the dibridged structures, the qualitative results obtained by CASSCF coincide with those obtained by CCSD(T) methodology. The results of CASSCF calculations are shown in Tables S1 and S2.

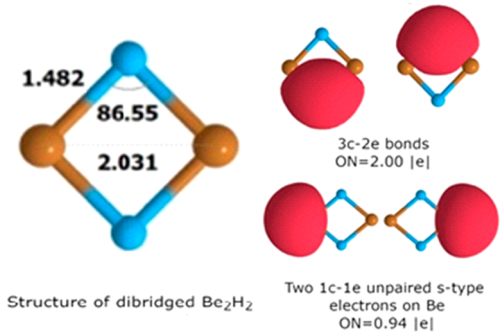

Figure 2. Chemical bonding pattern of dibridged Be_2H_2. ON denotes occupation numbers.

Mg_2H_2. The Mg_2H_2 molecule was observed in the laboratory by Wang and Andrews[14] in 2004. As in the case of Be_2H_2, only one vibrational fundamental was reported (1486 cm^{-1} for Mg_2H_2 and 1083 cm^{-1} for Mg_2D_2) and assigned to the linear HMg−MgH structure. In their study, Wang and Andrews also performed DFT calculations, predicting that the dibridged species lies 11 kcal/mol above the linear HMg−MgH. However, they do not assign any laboratory fundamentals to their rhomboid structure.

To study the behavior of the potential energy surface (PES) of Mg_2H_2, we also analyzed 10000 sample structures using the CK algorithm.[10] The optimized [CCSD(T)/cc-pVQZ level of theory] geometries may be found in Figure S2. Similar to Be_2H_2, the linear HMg−MgH structure is the global minimum. However, the other Mg_2H_2 structures lie much lower in energy than those for Be_2H_2. For example, the vinylidene-like structure lies only 4.0 kcal/mol above the global minimum, and the Mg···HMgH structure is 5.0 kcal/mol above linear HMg−MgH. The planar dibridged structure is also low-lying at 10.5 kcal/mol. As with the beryllium system, the monobridged Mg_2H_2 structure is a transition state between the vinylidene-like and HMg−MgH linear structure. The relative energy of the transition state is 25.2 kcal/mol, which is about 14 kcal/mol lower than that for Be_2H_2 structures. The chemical bonding for the Mg_2H_2 isomers is analogous to that for the Be_2H_2 structures and may be found in Figure S2. The relative energies of the Mg_2H_2 isomers are shown in Table 1.

Sr_2H_2 and Ba_2H_2. For the analogous strontium and barium systems, we used the CCSD(T) method with the cc-pVQZ-PP

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basis set using the *CFOUR* program.[15] For the Sr atom, the small-core pseudopotential of Hill and Peterson[16] was used with 28 core electrons. For the Ba atom, the inner 46 electrons were included in the small-core pseudopotential.

Our strontium predictions are related to the analogous calcium results[7] and are very different from those reported here for the beryllium and magnesium systems. Our results for Sr_2H_2 are shown in Table 1 and Figure 3. Like the calcium

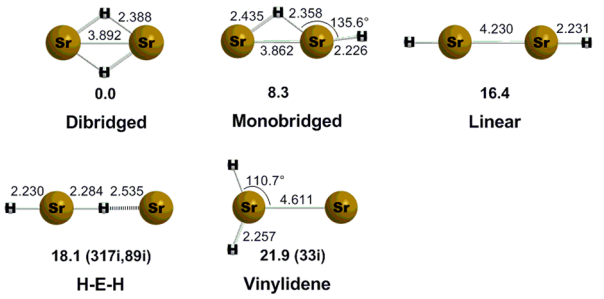

Figure 3. Geometries and energetics for the Sr_2H_2 stationary points at the CCSD(T)/cc-pVQZ-PP level. Bond distances are in angstroms and energies in kilocalories per mole. The imaginary vibrational frequencies (cm^{-1}), if any, are in the parentheses.

systems, the dibridged Sr_2H_2 structure is the global minimum. The dibridged structure is predicted to lie 16.4 kcal/mol *below* the linear structure. The monobridged Sr_2H_2 structure lies 8.1 kcal/mol *below* the conventional HSr−SrH linear structure.

In the excellent experimental study of calcium, strontium, and barium hydrides, Wang and Andrews[17] did not assign any observed vibrational features to Sr_2H_2. However, B3LYP computations on the dibridged, monobridged, and vinylidene-like structures of Sr_2H_2 were reported. Wang and Andrews predicted that the dibridged structure has the lowest energy, followed by the monobridged (3.4 kcal/mol) and vinylidene-like (14.7 kcal/mol) structures. The comparison with our results (Table 1) for the monobridged (8.3 kcal/mol above the dibridged) and vinylidene-like (21.9 kcal/mol) structures is reasonable considering their DFT methodology.

What are the best prospects for future experiments to identify Sr_2H_2 in the laboratory? Consider our theoretical vibrational frequencies and (especially) IR intensities reported in Tables 2 and 3. For the global minimum dibridged structure, the most intense IR feature is the Sr−H asymmetric stretching frequency (977 cm^{-1}, 122 km/mol). Although the monobridged structure lies 8.3 kcal/mol higher, the terminal Sr−H stretching fundamental (1176 cm^{-1}, 1118 km/mol) has a much greater IR intensity. Thus, a mass-selected IR spectrum might display both dibridged and monobridged structures.

Table 2. Vibational Frequencies (in cm^{-1}) and IR Intensities (in km/mol, in Parentheses) for the *Dibridged* E_2H_2 Structures (E = Sr, Ba) Predicted by the CCSD(T)/cc-pVQZ-PP Method

	symmetry	Sr_2H_2	Ba_2H_2
ring deformation $r_1 - r_2 + r_3 - r_4$	b_{3g}	941 (0)	905
ring deformation $r_1 - r_2 - r_3 + r_4$	b_{1u}	977 (122)	782
ring breath	a_g	896 (0)	774
ring deformation $r_1 + r_2 - r_3 - r_4$	b_{2u}	724 (69)	643
ring puckering	b_{3u}	362 (32)	262
E−E stretching	a_g	136 (0)	102

Table 3. Vibational Frequencies (in cm^{-1}) and IR Intensities (in km/mol, in Parentheses) for the *Monobridged* E_2H_2 Structures (E = Sr, Ba) Predicted by the CCSD(T)/cc-pVQZ-PP Method

	symmetry	Sr_2H_2	Ba_2H_2
E−H(terminal) stretching	a′	1176 (1118)	1077 (1922)
E−H(bridge) stretching (asym.)	a′	961 (113)	921 (137)
E−H(bridge) stretching (sym.)	a′	759 (573)	705 (302)
H−E−H bending	a′	187 (285)	173 (301)
E−H−E−H torsion	a″	104 (361)	19 (380)
E−E stretching	a′	97 (16)	70 (16)

The dibridged Sr_2H_2 structure has no permanent dipole moment and therefore will not be observable by microwave spectroscopy. However, the monobridged structure has a sizable dipole moment, 3.07 D. Predicted dipole moments and rotational constants may be seen in Table 4. The observation

Table 4. Dipole Moments (μ, in Debye) and Rotational Constants (A, B, and C, in Gigahertz) for the E_2H_2 Structures (E = Sr, Ba) Predicted by the CCSD(T)/cc-pVQZ-PP Method

molecule	structure	rotational constant (A, B, and C, GHz)	dipole moment ($\lvert\mu\rvert$, D)
Sr_2H_2	dibridged	130.93, 0.76, 0.76	0
	monobridged	241.48, 0.75, 0.75	3.074
	linear	0.61, 0.61, 0.00	0
	H−E−H	0.48, 0.48, 0.00	6.068
	vinylidene	56.26, 0.53, 0.52	10.143
Ba_2H_2	dibridged	127.58, 0.41, 0.41	0
	monobridged	206.40, 0.40, 0.40	3.061
	H−E−H	0.29, 0.29, 0.00	3.377
	linear	0.32, 0.32, 0.00	0
	cis	827.03, 0.32, 0.32	2.760
	vinylidene	55.46, 0.27, 0.27	12.741

of monobridged Sr_2H_2 by microwave spectroscopy would be a remarkable discovery. Moreover, this possibility is not so remote because precisely this was accomplished for monobridged Si_2H_2 in 1992 by Cordonnier and co-workers.[4]

The Ba_2H_2 system was treated theoretically in a manner analogous to that of Sr_2H_2, and the results are presented in Table 1 and Figure 4. The dibridged structure of Ba_2H_2 is again (like the valence isoelectronic calcium and strontium systems) the global minimum. The dibridged structure lies even further *below* (by 19.6 kcal/mol) the conventional HBa−

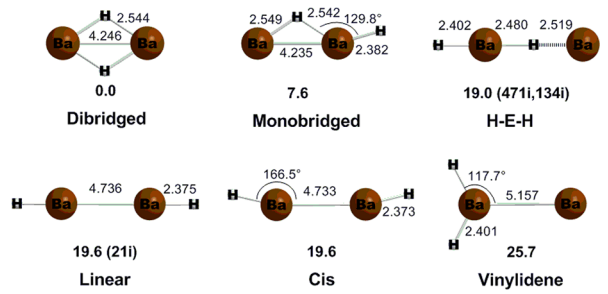

Figure 4. Geometries and energetics for the Ba_2H_2 stationary points at the CCSD(T)/cc-pVQZ-PP level. Bond distances are in angstroms and energies in kilocalories per mole. The imaginary vibrational frequencies (cm^{-1}), if any, are in the parentheses.

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BaH linear structure. Above the dibridged structure by 7.6 kcal/mol is the monobridged structure. Wang and Andrews[17] assigned no experimental vibrational features to Ba_2H_2 and reported no computations on the dibridged or monobridged structures.

As noted above, the dibridged structure is better described from a two-reference starting point. For this reason, CASSCF(6e,10o) computations were carried out with the cc-pVQZ-PP basis set for both the dibridged and monobridged structures. The results are in good agreement with the above CCSD(T) findings. The monobridged structure has a slightly lower energy, 5.4 kcal/mol, above the dibridged, compared to CCSD(T).

How do we propose that future experiments identify Ba_2H_2 in the laboratory? The dibridged ring deformation b_{1u} vibrational fundamental has a very large IR intensity (2394 km/mol) from the CASSCF(6e,10o)/cc-pVQZ-PP method. This feature should allow the dibridged structure to be observed. Although the monobridged structure is predicted to lie 7.6 kcal/mol above the dibridged global minimum, it may yet be observed in the laboratory. This is due to the large IR intensity of the monobridged terminal Ba−H stretch (1077 cm^{-1}), namely, 1922 km/mol.

As with Sr_2H_2, there is no microwave spectrum for the planar dibridged structure of Ba_2H_2 because of its lack of a permanent dipole moment. However, the monobridged Ba_2H_2 structure has a sizable dipole moment, namely, 3.06 D. Predicted dipole moments and rotational constants may be seen in Table 4. Thus, there is a hope that the monobridged Ba_2H_2 structure will be observed by microwave spectroscopy.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01651.

Computational methods, relative energies of E_2H_2 singlet species calculated at the CASSCF(6e,9o)/NEVPT2 level of theory (Table S1), relative energies (kcal/mol) of singlet and triplet dibridged E_2H_2 species calculated at the CASSCF(6e,9o)/NEVPT2 level of theory (Table S2), relative energies, optimized structures, and chemical bonding patterns for the five lowest isomers of Be_2H_2 (Figure S1), relative energies, optimized structures, and chemical bonding patterns for the five lowest isomers of Mg_2H_2 (Figure S2), and relative energies, optimized structures, and chemical bonding patterns for the five lowest isomers of Ca_2H_2 (Figure S3) (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Colegrove, B. T.; Schaefer, H. F. Dislyne (Si_2H_2) Revisited. *J. Phys. Chem.* **1990**, *94*, 5593−5602.

(2) Lischka, H.; Köhler, H.-J. *Ab Initio* Investigation of the Lowest Singlet and Triplet States of Si_2H_2. *J. Am. Chem. Soc.* **1983**, *105*, 6646−6649.

(3) Grev, R. S.; Schaefer, H. F. The Remarkable Monobridged Structure of Si_2H_2. *J. Chem. Phys.* **1992**, *97*, 7990−7999.

(4) Cordonnier, M.; Bogey, M.; Demuynck, C.; Destombes, J.-L. Nonclassical Structures in Silicon-Containing Molecules: The Monobridged Isomer of Si_2H_2. *J. Chem. Phys.* **1992**, *97*, 7984−7989.

(5) Lein, M.; Krapp, A.; Frenking, G. Why do the Heavy-Atom Analogues of Acetylene E_2H_2 (E = Si-Pb) Exhibit Unusual Structures? *J. Am. Chem. Soc.* **2005**, *127*, 6290−6299.

(6) Mukherjee, D.; Schuhknecht, D.; Okuda, J. Hydride Complexes of Calcium: A New Family of Molecular Alkaline-Earth-Metal Compounds. *Angew. Chem., Int. Ed.* **2018**, *57*, 9590−9602.

(7) Bowman, M. C.; Douberly, G. E.; Schaefer, H. F. Convergent Energies and Anharmonic Vibrational Spectra of Ca_2H_2 and Ca_2H_4 Constitutional Isomers. *Phys. Chem. Chem. Phys.* **2019**, *21*, 10914−10922.

(8) Tague, T. J.; Andrews, L. Reactions of Beryllium Atoms with Hydrogen. Matrix Infrared Spectra of Novel Product Molecules. *J. Am. Chem. Soc.* **1993**, *115*, 12111−12116.

(9) Lundell, K. A.; Boldyrev, A. I. Tug of War Between Classical and Multicenter Bonds in H-$(Be)_n$-H Species. *Chem. Phys. Lett.* **2018**, *699*, 85−87.

(10) Sergeeva, A. P.; Averkiev, B. B.; Zhai, H.-J.; Boldyrev, A. I.; Wang, L.-S. All-Boron Analogues of Aromatic Hydrocarbons:B_{17}^- and B_{18}^-. *J. Chem. Phys.* **2011**, *134*, 224304 See also:. Bera, P. P.; Sattelmeyer, K. W.; Saunders, M.; Schaefer, H. F.; Schleyer, P. R. Mindless Chemistry. *J. Phys. Chem. A* **2006**, *110*, 4287−4290.

(11) (a) Zubarev, D. Y.; Boldyrev, A. I. Developing Paradigms of Chemical Bonding: Adaptive Natural Density Partitioning. *Phys. Chem. Chem. Phys.* **2008**, *10*, 5207−5217. (b) Tkachenko, N. V.; Boldyrev, A. I. Chemical Bonding Analysis of Excited States Using the

Adaptive Natural Density Partitioning Method. *Phys. Chem. Chem. Phys.* **2019**, *21*, 9590−9596.
(12) F., Neese *The ORCA Program System*, version 4.0; Wiley Intersdisc. Rev., 2017; Vol. *8*, p e1327.
(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B., et al. *Gaussian 16*, revision B01; Gaussian Inc.: Wallingford, CT, 2016.
(14) Wang, X.; Andrews, L. Infrared Spectra of Magnesium Hydride Molecules, Complexes, and Solid Magnesium Dihydride. *J. Phys. Chem. A* **2004**, *108*, 11511−11520.
(15) *CFOUR: a quantum chemical program package* written by Stanton, J. F.; Gauss, J.; Harding, M. E.; Szalay, P. G., with contributions from A. A. Auer, et al., with the integral packages *MOLECULE* (J. Almlöf and P. R. Taylor), *PROPS* (P. R. Taylor), *ABACUS* (T. Helgaker, H. J. Aa. Jensen, P. Jorgensen, and J. Olsen), and ECP routines by A. V. Mitin and C. van Wullen, 2010.
(16) Hill, J. G.; Peterson, K. A. Gaussian Basis Sets for Use in Correlated Molecular Calculations. XI. Pseudopotential-Based and All-Electron Relativistic Basis Sets for Alkali Metals (K-Fr) and Alkaline Earth (Ca-Ra) Elements. *J. Chem. Phys.* **2017**, *147*, 244106.
(17) Wang, X.; Andrews, L. Metal Dihydride (MH_2) and Dimer (M_2H_4) Structures in Solid Argon, Neon, and Hydrogen (M = Ca, Sr, and Ba): Infrared Spectra and Theoretical Calculations. *J. Phys. Chem. A* **2004**, *108*, 11500−11510.

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