Theoretical prediction of the vibrational spectra of group IB trimers

(diatomics-in-molecules/molecular structure)

STEVEN C. RICHTSMEIER*, JAMES L. GOLE†, AND DAVID A. DIXON*

*Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455; and †Department of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

Communicated by Bryce Crawford, Jr., July 25, 1980

ABSTRACT The molecular structures of the group IB trimers, Cu₃, Ag₃, and Au₃, have been determined by using the semi-empirical diatomics-in-molecules theory. The trimers are found to have C_{2v} symmetry with bond angles between 65° and 80°. The trimers are bound with respect to dissociation to the asymptotic limit of an atom plus a diatom. The binding energies per atom for Cu₃, Ag₃, and Au₃ are 1.08, 0.75, and 1.16 eV, respectively. The vibrational frequencies of the trimers have been determined for comparison with experimental results. The vibrational frequencies are characterized by low values for the bending and asymmetric stretch modes. The frequency of the symmetric stretch of the trimer is higher than the stretching frequency of the corresponding diatomic. A detailed comparison of the theoretical results with the previously measured Raman spectra of matrix isolated Ag₃ is presented.

The structures of small metal clusters are of wide interest (1-8). With the goal of spectroscopic characterization, naked metal clusters in the absence of ligands are now being produced in the gas phase (9-12) and through diffusion-controlled clustering in rare gas matrices (13-19). Although these experimental studies can provide detailed structural information, progress has been slowed by difficulties in making and correlating the measurements. The electronic structure of small metal clusters is under active study by a number of theoretical groups (20-37). Diverse methods from extended Hückel to *ab initio* calculations have been applied, leading to multifarious conclusions. In many cases there may be considerable uncertainty regarding the level of sophistication that must be used to correctly describe and interpret the problem.

Recently, Schulze *et al.* (18) have generated the molecules (Ag)_n in rare gas matrices and measured Raman spectra which they assign to Ag₂ and Ag₃ for low metal/matrix ratios. From their measurements, these authors concluded that Ag₃ has a linear structure, in agreement with the complete neglect of differential overlap (CNDO) calculations of Baetzold (34, 35). We have been concerned with the electronic structure of metal clusters that are formed from the interaction of metal atoms with one unpaired valence electron in an *s* orbital; hence, our focus has been on the alkali (group IA) and coinage (group IB) metals. In order to describe these relatively simple atoms, we have used the diatomics-in-molecules (DIM) method (38-42) which has its basis in the valence bond formalism. As an aid to interpreting the Raman data, we have studied the trimers of the group IB metals in order to predict their structure and the energetics of their molecular vibrations.

The publication costs of this article were defrayed in part by page charge payment. This article must therefore be hereby marked "advertisement" in accordance with 18 U. S. C. §1734 solely to indicate this fact.

METHOD

The DIM method that we use is based on the Heitler-London approximation (43). For the triatomic systems of interest, the energies of the covalent doublet states are given by the London equation

$$E = J_{12} + J_{13} + J_{23} \pm 2^{-1/2} [(K_{12} - K_{13})^2 + (K_{12} - K_{23})^2 + (K_{13} - K_{23})^2]^{1/2} \quad [1]$$

in which J_{ij} and K_{ij} are the Coulomb and exchange integrals between atoms *i* and *j*. We evaluate J_{ij} and K_{ij} from

$$J_{ij} = \frac{1}{2} [{}^1\Sigma_{ij}(R_{ij}) + {}^3\Sigma_{ij}(R_{ij})] \quad [2]$$

$$K_{ij} = \frac{1}{2} [{}^1\Sigma_{ij}(R_{ij}) - {}^3\Sigma_{ij}(R_{ij})]$$

in which ${}^1\Sigma_{ij}(R_{ij})$ corresponds to the potential curve for the ground electronic state of the diatomic at the distance R_{ij} between atoms *i* and *j* and ${}^3\Sigma_{ij}(R_{ij})$ corresponds to the lowest triplet curve which is generally repulsive. The singlet and triplet curves correlate in the asymptotic limit to the ground ²S states of atoms *i* and *j*. If we consider expressions 2, it is apparent that there are two distinct advantages and one notable difficulty in the application of DIM to Cu, Ag, and Au. The first advantage is the obvious computational efficiency obtained in the application of DIM. The second is the inclusion of relativistic effects inherent in the use of empirical singlet potential curves. These effects can be significant for Au and other atoms in the third transition row (44). In general the triplet curves needed for the DIM calculation are not experimentally determined and must be obtained from a theoretical calculation. Here we have an inherent difficulty.

The DIM method which we describe will be suitable for the group IB trimers only if the dominant atomic states have the ground state configuration *d*¹⁰*s*¹. The *d*⁹*s*² states of Cu, Ag, and Au are located 1.39, 3.75, and 1.14 eV, respectively, above the ground electronic state (45). Thus, DIM should represent a useful approximate for the study of the trimers.

The DIM method has been applied to a number of systems (22-25, 38-42, 46, 47). Indeed, some of the earliest applications of the DIM approach involved the study of crystalline metals (46). Recently, the technique has been applied to the characterization of hydrogen clusters. For the H₃ (41) and H₆ (42) systems, one finds good agreement between DIM and *ab initio* studies; however, for H₄ (47) the correlation is poor. Because the hydrogenic species are unstable relative to their asymptotic limits, DIM calculations may yield significantly different results for the stable group IB metals. Therefore, we have checked the

Abbreviation: DIM, diatomic-in-molecules.

method on the trimers Li_3 and Na_3 which are bound with respect to the limit $M + M_2$ and for which good *ab initio* calculations are available (26–31). The potential curves of the singlet and triplet states of Li_2 and Na_2 used in these calculations are given in Table 1. These results are summarized in Table 2. Both the binding energies and structures predicted by the DIM method are in reasonable agreement with the *ab initio* calculations. Although DIM predicts bond angles that are slightly too large, it is apparent that we are not overestimating the stability of strongly bent molecules, a problem present in recent calculations on H_4 .

CALCULATIONS ON GROUP IB METALS

Potential Curves. The choice of potential curves for the group IB diatomic was aided by the elegant pseudopotential calculations of Ermler *et al.* (48). The singlet curves were generated with Morse potentials by using experimental parameters (49). The triplet curve for Au_2 was fit to a Lennard–Jones 6- n potential (50) and the value of n was optimized to 12. The experimental (51) and theoretical equilibrium internuclear distances determined for Au_2 differ slightly. Therefore, we have scaled the position of the triplet minimum with respect to the singlet minimum. The difference between the singlet and triplet minima is assumed to be a constant, the position of the triplet minimum being set with respect to the experimental singlet minimum. Calculations were also carried out by using the theoretically determined singlet curve for Au_2 . The results for a large variety of clusters of Au were similar to those obtained with the experimental singlet curves, except for slight differences in bond length and binding energy. This is not surprising, because these properties directly reflect the parameters for the singlet state. The Ag_2 and Cu_2 theoretical curves do not agree as well with experiment as does the Au_2 curve. Therefore, we used the experimental singlet curves (52) and scaled the triplet curves as described above. The forms and values for these curves for the group IB dimers are summarized in Table 1.

The results of our DIM calculations on the group IB trimers are reported in Table 3 and depicted graphically in Figs. 1 and 2. The ground states of Cu_3 , Ag_3 , and Au_3 are of C_{2v} geometry with bond angles between 65° and 80° . These states are all of $^2\text{B}_2$ symmetry. The trimer bond lengths are longer than the respective bond length in the dimer. The trimers are all bound with respect to dissociation to monomer and dimer, with Cu_3 and Au_3 showing a much larger dissociation energy. This trend in bond energies is also observed in the homonuclear diatomics [$D_0^0(\text{Ag}_2) < D_0^0(\text{Cu}_2) \approx D_0^0(\text{Au}_2)$] and may be related to the relative energies of the $d^{10}s^1$ and d^9s^2 atomic configurations.

We have also geometry-optimized structures corresponding to D_{3h} (equilateral triangle) and $D_{\infty h}$ (linear structure) sym-

Table 1. Parameters for singlet and triplet curves used in DIM calculations

Atom	1D , eV	β , a.u. $^{-1}$	r_e , a.u.	3D , eV	σ , a.u.
Li	1.07	0.4571	5.049	0.02721	6.939
Na	0.73	0.4531	5.817	0.02721	7.266
Cu	1.98	0.7616	4.195	0.2349	4.149
Ag	1.63	0.7924	4.724	0.0513	5.507
Au*	2.24	0.9087	4.5068	0.16245	4.843
Au†	2.265	0.80455†	4.50	0.16245	4.675

Singlet curve (Morse potential curve): $^1E(r_{ij}) = ^1D[\exp\{-2\beta(r_{ij} - r_e)\} - 2\exp\{-\beta(r_{ij} - r_e)\}]$. Triplet curve (Lennard–Jones potential curve) $^3E(r_{ij}) = 4^3D[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6]$

* Theoretical curves for Au_2 .

† Experimental singlet curves for Au_2 .

‡ For $r_{ij} > 5.75$ a.u. For $r \leq 5.75$ a.u. use $\beta = 0.8425$ a.u. $^{-1}$.

Table 2. Comparison of *ab initio* and DIM results for Li_3 and Na_3

Method	Binding energy*	R_e †	θ_e ‡	Reference
Li_3				
<i>ab initio</i>	34.0	2.77	71	30
<i>ab initio</i>	33.6	2.84	73	27
<i>ab initio</i>	29.4	2.80	68	28
<i>ab initio</i>	28.7	2.96	74	31
DIM	33.0	2.94	92	This work
Na_3				
<i>ab initio</i>	26.2	3.55	75	29
DIM	23.7	3.26	86	This work

* In kcal/mol (1 cal = 4.184 J) relative to dissociation to three atoms.

† Equilibrium bond length in Å.

‡ Equilibrium bond angle in degrees.

metry. The appropriate parameters are given in Table 3. For Cu_3 , the D_{3h} structure lies close in energy to the C_{2v} $^2\text{B}_2$ configuration, whereas the linear form is unstable by 4.2 kcal/mol (1 cal = 4.184 J). For Ag_3 , the linear form is close in energy to the bent C_{2v} form and the D_{3h} structure shows the least stability. For Au_3 , the $D_{\infty h}$ and D_{3h} forms are both unstable by approximately 3.5 kcal/mol relative to the C_{2v} geometry. The D_{3h} geometries are of ^2E symmetry and must undergo a Jahn–Teller distortion (54, 55). As predicted by the Jahn–Teller theorem, Fig. 2 demonstrates that the DIM method does show a kink in the bending mode at $\theta = 60^\circ$. If this region is important for potential surface considerations, other methods beyond the Born–Oppenheimer approximation must be used to treat the conical intersection at 60° (56). Although the group IB trimers do appear to have C_{2v} geometries, we expect them to be quite fluxional. This fluxionality may play an important role in bending mode considerations, especially in view of possible Jahn–Teller distortions.

Vibrational Level Structure. In order to predict the vibrational level structure for the trimers, we have determined the energy surface for each of the “simple” normal modes corresponding to the symmetric (ω_1) and asymmetric (ω_3) stretch and the bending potential (ω_2). Because the interpretation of recent laser Raman studies on Ag represents a major consideration of this study, the appropriate surfaces are plotted for Ag_3

Table 3. Physical properties of group IB trimers

Property*	Cu	Ag	Au
R_e , Å	2.28	2.64	2.53
θ_e , degrees	65.6	76.6	69.3
Binding energy, eV†	1.25	0.61	1.23
Binding energy/atom, eV	1.08	0.75	1.16
Cohesive energy, eV‡	3.50	2.96	3.78
Binding energy/atom, eV§	1.07	0.68	1.10
Binding energy/atom, eV¶	1.01	0.74	1.11
ω_1 , cm^{-1}	445.0	264.5	276.4
ω_2 , cm^{-1}	138.2	36.4	56.6
ω_3 , cm^{-1}	163.5	65.1	143.0
R_e (dimer), Å	2.22	2.50	2.47
ω_e (dimer), cm^{-1}	265	192	191
D_e (dimer), eV	1.99	1.64	2.25

* R_e , equilibrium bond distance; θ_e , equilibrium bond angle; ω , frequency; D , dissociation energy.

† Energy relative to atom plus diatomic.

‡ From ref. 53.

§ Binding energy for equilateral triangle structure (D_{3h}).

¶ Binding energy for linear structure ($D_{\infty h}$).

FIG. 1. Potential curves for the simple modes of Ag_3 . (A) Symmetric stretch (ω_1); (B) bend (ω_2) (note the change in energy units for this mode as compared to ω_1 and ω_3); (C) asymmetric stretch (ω_3) (only half of the curve is shown). The value of R corresponds to increasing a Ag—Ag bond length. A corresponding decrease in the other bond length is not shown.

in Fig. 1. The surfaces for ω_1 and ω_3 are found to be similar for all the group IB trimers; however, there are significant differences for the potential functions describing the bending modes of Cu, Ag, and Au. Therefore, plots for the bending potentials are presented in Fig. 2. The ω_1 and ω_2 modes are of the same symmetry (A_1) and may be coupled whereas the ω_3 mode (B_2) is singular. The force constants corresponding to the "simple" modes were calculated by using a one-dimensional quantum mechanical method (57). The force constants determined for the simple ω_1 mode were characterized by an extremely small anharmonicity. That is, the ω_1 potential (Fig. 1) is very close to harmonic. The ω_1 and ω_2 motions (force constants) were combined in a normal coordinate F-G analysis (58, 59) to obtain a final set of frequencies. Examination of the L matrix showed a small mixing of pure bend and pure stretch to form the resultant coupled normal modes. The frequencies determined

by using the procedure outlined above are reported in Table 3. In all cases we find the ordering $\omega_1 > \omega_2 > \omega_3$. The ω_3 curves are very anharmonic in their lower regions as a result of the "bucket-like" nature of these potentials. If the zero point energy for the ground state of Ag_3 is placed at $0.5 h\nu$, the fundamental ($v = 0$ to $v = 1$) infrared absorption has an energy corresponding to $1.25 h\nu$ and the $v = 2$ level is at $3.5 h\nu$. Above $v = 2$, the ω_3 potential appears to be only slightly anharmonic. A similar behavior is found for the ω_2 potentials with the most pronounced anharmonic effects being those for Ag_3 . It is also of note that ω_2 and ω_3 for Ag_3 and ω_2 for Au_3 all fall well below 100 cm^{-1} .

In their observation of a weak laser Raman spectra associated with silver compounds formed in a rare gas matrix, Schulze *et al.* (18) assigned two major scattering features at 194 ± 0.5 and $120.5 \pm 0.5 \text{ cm}^{-1}$ to Ag_2 and Ag_3 , respectively. This assignment

FIG. 2. Comparison of potential curves for ω_2 for the three metallic trimers (A) Cu_3 ; (B) Ag_3 ; (C) Au_3 .

was based in large part on the growth characteristics of the Raman bands observed as a function of increased Ag concentration in the matrix. At intermediate metal/matrix concentrations, the band at 194 cm^{-1} is relatively weak, bands at 170, 120.5, and 93 cm^{-1} have totally disappeared, and a band at 203 cm^{-1} is of intensity comparable to that at 194 cm^{-1} . In addition, new bands at 151, 107, and 73 cm^{-1} have developed. The band at 194 cm^{-1} is assigned to Ag dimer through comparison with the known gas phase spectrum. Based upon their correlation of growth profiles, Schulze *et al.* (18) reasoned that only the 120.5 cm^{-1} band can be assigned to Ag_3 . On the basis of this "lone" strong Raman absorption for the trimer, these authors assign a linear structure to Ag_3 , reasoning that a D_{3h} (2 bands) or C_{2v} (3 bands) geometry should lead to multiple strong Raman bands. Our calculations predict a C_{2v} geometry and therefore we expect to observe three Raman bands. Further, the unusually high anharmonicities that characterize the trimer normal modes conceivably can lead to considerable combination, difference, and overtone structure. The intensities of some of the resulting bands may be comparable to or in some cases greater than the intensity of the fundamental absorptions. In view of these possibilities and the already weak nature of the laser Raman spectrum observed by Schulze *et al.* (18), we suggest some alternate assignments for those features observed in the Raman spectrum.

From our calculations, it is apparent that the value of ω_1 , the trimer symmetric stretch, considerably exceeds the Ag dimer frequency. This result also holds for Cu and Au. Unfortunately, it does not appear that the published Raman data extend to this spectral region. Because of the intense and broad nature of the exciting laser line, it is difficult to observe Raman Stokes shifts at frequencies less than 100 cm^{-1} from the laser line.

Our calculations predict that it may not be possible to observe and definitely identify the Raman band corresponding to the bending mode fundamental of Ag_3 . If we assign an accuracy of $\pm 20\%$ to our calculated frequencies, the 70 cm^{-1} feature observed by Schulze *et al.* at high metal/matrix ratios may correspond to the fundamental for the asymmetric stretch ($\omega_{\text{calc}} = 65\text{ cm}^{-1}$). There is reason to search out intense combination tones in the Raman spectrum of Ag_3 . Although overtones and combination tones are relatively weak in a typical nonresonant Raman study, the ω_2 and ω_3 potentials are unusually anharmonic. This rather novel behavior coupled with the fluxional nature of the group IB trimers may lead to strong combination tones. A further intriguing aspect of the Raman experiments arises if we consider that the laser source promotes some local heating of the matrix (18). Because of the extremely low frequency associated with the Ag_3 bending mode, localized heating will lead to a substantial population in various levels of the ω_2 potential. As a result, the Raman spectrum may be characterized by anti-Stokes combination tones involving ω_2 . Similar comments can be made regarding ω_3 although the effects would not be expected to be as pronounced.

In the light of our previous remarks regarding anharmonic potentials, the bands observed by Schulze *et al.* (18) at 151 and 107 cm^{-1} are particularly intriguing. These two bands, which dominate the spectrum at high metal/matrix ratios, vary in unison as the conditions of matrix preparation are varied. From our calculations, it would not be unreasonable to assign the 107 cm^{-1} feature to the combination tone $\omega_2 + \omega_3$ ($\nu_{\text{calc}} = 101\text{ cm}^{-1}$). If ω_2 is slightly larger than calculated (42 cm^{-1}), the 151 cm^{-1} feature might also be associated with $2\omega_2 + \omega_3$. Similarly, this feature might correspond to $2\omega_3$. Thus, the dominant features in an overall weak Raman spectrum can be correlated with combination tones involving the very low frequency bending or stretching modes. Of course, the band at 120.5 cm^{-1}

might also be attributed to a combination tone ($\omega_2 + \omega_3$) within the accuracy of our calculated frequencies.

The significance of the previous exercise is its demonstration that several bands observed by Schulze *et al.* (18) in their laser Raman study may be correlated with Ag_3 normal mode combination tones. Because two low-frequency modes are associated with Ag_3 , the analysis of this trimer spectrum may be ambiguous and it is not difficult to find features which could be associated with a C_{2v} structure. Ozin *et al.* (19) have studied the photochemistry of Ag_3 in Ar, Kr, and Xe matrices. They interpret their findings in terms of a "photoisomerization" process between two forms of Ag_3 . It appears that bulk thermal annealing of the matrix at 25 K for 5 min regenerates the initial form of Ag_3 from the photoisomer. This low temperature required for isomerization is consistent with our values for the small energy difference between the bent (C_{2v}) and linear forms of Ag_3 .

Our calculations suggest that Cu_3 represents a much better subject for Raman or infrared study. This group IB trimer is characterized by normal modes corresponding to significantly larger frequencies, all of which are well separated from the dimer frequency. Finally, we should note that the presence of a low-frequency bending mode may lead to ambiguity in the analysis of Au_3 spectra.

Further Properties. The current results demonstrate a number of interesting properties which characterize the group IB series, not the least of which are the significant dissociation energies determined for the trimers. Other determinations of group IB trimer structure have involved semi-empirical theories such as extended Hückel (60) or complete neglect of differential overlap (61) which follow a molecular orbital approach. These methods predict that Cu_3 and Ag_3 are linear. However, the extended Hückel calculations (33) significantly underestimate the dissociation energy of Cu_3 to monomer plus dimer, finding 12 kcal/mol compared to our value of 29.2 kcal/mol. The complete neglect of differential overlap (33, 34) results for Ag_3 also underestimate the binding energy, predicting 5.9 kcal/mol compared to the DIM value of 14.5 kcal/mol. The binding energy per atom can be related to bulk metallic properties through comparison with the cohesive energy (61). The binding energies per atom from our calculations are 25.0, 17.4, and 26.7 kcal/mol for Cu, Ag, and Au, respectively. These values should be compared to the cohesive energies of 80.8, 68.3, and 87.3 kcal/mol (53). Although significant binding is present in the trimer, it is still far from the cohesive energy.

The variation of the binding energies predicted by the three methods can be explained from simple considerations. The argument is similar to that put forth by Cashion and Herschbach (41) to explain the barrier in H_3 and by Dixon *et al.* (42) to explain the stability of other hydrogen clusters. For simplicity, we discuss the linear form, for which destabilizing terms result from a repulsive triplet interaction between the end atoms. Thus, the general form of the triplet curve is important for the correct description of the stabilization energy. A comparison of the *ab initio* curve for Cu_2 used in our study and the triplet curve given by the extended Hückel treatment (33) demonstrates why the extended Hückel method predicts such a weak binding energy. The triplet curve from the extended Hückel calculation is significantly more repulsive than the more accurate *ab initio* curve in the important region $r > R_e(\text{Cu}_2)$. This leads to a lower binding energy. By way of comparison, for $r < [R_e(\text{Cu}_2) - 0.5\text{ \AA}]$ the curves determined by the two methods provide a similar prediction of the repulsive wall.

In summary, the current calculations predict that the group IB trimers have C_{2v} structures. However, they are quite fluxional and the $D_{\infty h}$ structure lies only slightly higher in energy.

At bond angles in excess of 120° , the bending curves are extremely flat, showing a large change in bond angle for a very small change in energy. The predicted positions of the vibrational peaks have been compared with the experimental spectra. These results show that much care must be taken in interpreting matrix isolation spectra when a number of aggregates are present. If there is an accidental degeneracy in the values of spectral frequencies, and multimode features are not carefully considered, erroneous conclusions concerning molecular structure can be reached. We emphasize that such equivalencies may not allow one to use the cluster growth method as a means of assigning bands to particular molecular species.

We thank Prof. W. C. Ermler for transmitting unpublished details of his potential curves. This work was partially supported by National Science Foundation Grant CHE-7905985 (D.A.D.). D.A.D. was A. P. Sloan Foundation Fellow (1977–1979), Camille and Henry Dreyfus Teacher-Scholar (1978–1983), and DuPont Young Faculty Grantee (1978).

1. Robinson, A. L. (1974) *Science* **185**, 772–774.
2. Demitras, G. C. & Muetterties, E. L. (1977) *J. Am. Chem. Soc.* **99**, 2796–2797.
3. Sinfelt, J. H. (1977) *Acc. Chem. Res.* **10**, 15–20.
4. Muetterties, E. L. (1977) *Science* **196**, 839–848.
5. Muetterties, E. L. (1975) *Bull. Soc. Chim. Belg.* **84**, 959–986.
6. Muetterties, E. L. (1976) *Bull. Soc. Chim. Belg.* **85**, 451–470.
7. Muetterties, E. L., Rhodin, T. N., Band, E., Brucker, C. F. & Pretzer, W. R. (1979) *Chem. Rev.* **79**, 91–137.
8. Band, E. & Muetterties, E. L. (1978) *Chem. Rev.* **78**, 639–658.
9. Preuss, D. R., Pace, S. A. & Gole, J. L. (1979) *J. Chem. Phys.* **71**, 3553–3560.
10. Herrmann, A., Schumaker, E. & Wöste, L. (1978) *J. Chem. Phys.* **68**, 2327–2336.
11. Herrmann, A., Leutwyler, S., Schumaker, E. & Wöste, L. (1978) *Helv. Chim. Acta* **61**, 453–487.
12. Leutwyler, S. & Schumaker, E. (1975) *Chimia* **31**, 475–478.
13. Moskovits, M. & Ozin, G. A. (1976) *Crytochemistry* (Wiley, New York).
14. Ozin, G. A. (1977) *Catal. Rev. Sci. Eng.* **16**, 191–230.
15. Ozin, G. A. & Huber, H. (1978) *Inorg. Chem.* **17**, 155–163.
16. Moskovits, M. & Hulse, J. E. (1977) *J. Chem. Phys.* **67**, 4271–4278.
17. Lindsay, D. M., Herschbach, D. R. & Kwiram, A. L. (1976) *Mol. Phys.* **32**, 1199–1213.
18. Schulze, W., Becker, H. U., Minkwitz, R. & Manzel, K. (1978) *Chem. Phys. Lett.* **55**, 59–61.
19. Ozin, G. A., Huber, H. & Mitchell, S. A. (1979) *Inorg. Chem.* **18**, 2932–2934.
20. Schaeffer, H. F., III (1977) *Acc. Chem. Res.* **10**, 287–293.
21. Bauschlicher, C., Jr., Bagus, P. & Schaeffer, H. F., III (1978) *IBM J. Res. Dev.* **22**, 213–220.
22. Companion, A. L., Steible, D. J. & Starshak, A. J. (1968) *J. Chem. Phys.* **49**, 3637–3640.
23. Companion, A. L. (1978) *Chem. Phys. Lett.* **56**, 500–502.
24. Pickup, B. T. (1973) *Proc. R. Soc. London Ser. A* **333**, 69–87.
25. Gelb, A., Jordan, K. D. & Silbey, R. (1975) *Chem. Phys.* **9**, 175–182.
26. Davies, D. W. & del Conde, G. (1977) *Mol. Phys.* **33**, 1813–1814.
27. Bagus, P. S., del Conde, G. & Davies, D. W. (1977) *Faraday Spec. Discuss. Chem. Soc.* **62**, 321.
28. Kendrick, J. & Hillier, I. H. (1977) *Mol. Phys.* **33**, 635–640.
29. Martin R. L. & Davidson, E. R. (1978) *Mol. Phys.* **35**, 1713–1729.
30. Gerber, W. H. & Schumaker, E. (1978) *J. Chem. Phys.* **69**, 1692–1703.
31. Gole, J. L., Childs, R., Dixon, D. A. & Eades, R. A. (1980) *J. Chem. Phys.* **72**, 6368–6375.
32. Fripiat, J. G., Chow, K. T., Boudart, M., Diamond, J. R. & Johnson, K. H. (1975) *J. Mol. Catal.* **1**, 59–72.
33. Anderson, A. B. (1977) *J. Chem. Phys.* **66**, 5108–5111.
34. Baetzold, R. C. (1971) *J. Chem. Phys.* **55**, 4355–4370.
35. Baetzold, R. C. (1976) *Adv. Catal.* **25**, 1–55.
36. Goddard, W. A., Walch, S. P., Kappe, A. K., Upton, T. H. & Melius, C. F. (1977) *J. Vac. Sci. Technol.* **14**, 416–418.
37. Bachman, C., Demuynk, J. & Veillard, A. (1978) *Gazz. Chim. Ital.* **108**, 389–391.
38. Kunz, P. J. (1979) in *Atom-Molecule Collision Theory*, ed. Bernstein, R. B. (Plenum, New York), pp. 79–110.
39. Tully, J. C. (1977) in *Modern Theoretical Chemistry: Semi-Empirical Methods of Electronic Structure Calculations*, ed. Segal, G. A. (Plenum, New York), Vol. 7B, pp. 173–200.
40. Ellison, F. O. (1963) *J. Am. Chem. Soc.* **85**, 3540–3544.
41. Cashion, J. K. & Herschbach, D. R. (1964) *J. Chem. Phys.* **40**, 2358–2363.
42. Dixon, D. A., Stevens, R. M. & Herschbach, D. R. (1977) *Faraday Spec. Discuss. Chem. Soc.* **62**, 110–126.
43. Glasstone, S., Laidler, K. J. & Eyring, H. (1941) *The Theory of Rate Processes* (McGraw-Hill, New York).
44. Pitzer, K. S. (1979) *Acc. Chem. Res.* **12**, 271–275.
45. Moore, C. E. (1949) *Atomic Energy Levels*, NBS Circular No. 467 (U.S. Government Printing Office, Washington, DC), Vols. 1 and 2.
46. Taylor, H. S., Eyring, H. & Sherman, A. (1933) *J. Chem. Phys.* **1**, 68–76.
47. Eaker, C. W. & Parr, C. A. (1976) *J. Chem. Phys.* **65**, 5155–5160.
48. Ermler, W. C., Lee, Y. S. & Pitzer, K. S. (1979) *J. Chem. Phys.* **70**, 293–298.
49. Herzberg, G. (1950) *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, NJ), 2nd Ed.
50. Hirschfelder, J. O., Curtiss, C. F. & Bird, R. B. (1954) *Molecular Theory of Gases and Liquids* (Wiley, New York).
51. Ames, L. L. & Barrow, R. F. (1967) *Trans. Faraday Soc.* **63**, 39–44.
52. Verhaegen, G., Stafford, F. E., Goldfinger, P. & Ackerman, M. (1962) *Trans. Faraday Soc.* **58**, 1926–1938.
53. Kittel, C. (1971) *Introduction to Solid State Physics* (Wiley, New York), 4th Ed.
54. Jahn, H. A. & Teller, E. (1937) *Proc. R. Soc. London Ser. A* **161**, 220–235.
55. Mead, C. A. (1980) *Chem. Phys.*, **49**, 23–38.
56. Mead, C. A. & Thruhar, D. G. (1979) *J. Chem. Phys.* **70**, 2284–2296.
57. Thruhar, D. G. (1972) *J. Comp. Phys.* **10**, 123–132.
58. Wilson, E. B., Jr., Decius, J. C. & Cross, P. C. (1955) *Molecular Vibrations* (McGraw-Hill, New York).
59. Blanke, J. F. & Overend, J. (1978) in *Vibrational Spectra and Structure*, ed. Durig, J. R. (Elsevier, Amsterdam), Vol. 7, pp. 270–315.
60. Hoffman, R. & Lipscomb, W. N. (1962) *J. Chem. Phys.* **36**, 3489–3493.
61. Pople, J. A. & Beveridge, D. L. (1970) *Approximate Molecular Orbital Theory* (McGraw-Hill, New York).