275 and 200 cm^{-1}, respectively.[3] The appearance in the C_2D_4 spectrum of the torsional vibration, which is not totally symmetric under C_{2v}, can be taken as an indication that the excited state may not be exactly in the eclipsed form, but rather slightly staggered.

In conclusion, the essence of the preceding analysis is that the vibrational structure of the electronic absorption spectra of C_2H_4 and C_2D_4 may be more readily consistent with an almost eclipsed, nonplanar structure for the first excited-singlet electronic state of ethene than with the merely twisted structure previously postulated from theoretical considerations.[6]

[1] R. McDiarmid and E. Charney, J. Chem. Phys. **47**, 1517 (1967).

[2] There are several inconsistent values of frequency differences in Tables I and II of Ref. 1. As the stated average frequencies of that article can be computed only by using these inconsistent values and as they have been deduced to be inconsistent because of the crosscheck in the various columns of the tables, these values are presumed not to represent typographical errors. Apart from five minor errors noted, the serious error in the difference ΔG^1 of the two members 52427 and 53123 of the primary progression of C_2H_4, 796 instead of the correct magnitude 696, means that all later treatment of Ref. 1 is inaccurate quantitatively if not qualitatively.

[3] G. Herzberg, *Infra-red and Raman Spectra* (D. Van Nostrand Co., Inc., Princeton, N.J., 1960).

[4] A. D. Walsh, J. Chem. Soc. **1953**, 2325.

[5] F. G. Baglin, S. F. Bush, and J. R. Durig, J. Chem. Phys. **47**, 2104 (1967).

[6] R. S. Mulliken, Phys. Rev. **41**, 751 (1932).

Comment on "Electron in Box Theory for Metal-Atom Clusters"

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I have noted certain errors of calculation in Libby's paper on the application of the electron in box model to the metal-atom cluster compounds.[1] The corrected table (agreed to by Professor Libby by correspondence) is given, together with a comparison of Libby's original numbers,[1] in Table I. It is to be noted that the distribution of the numbers of electrons actually found in stable clusters (the italicized numbers 12, 16, 18, 24, 26, and 32) is very different in both cases.

TABLE I. Numbers of electrons to fill to successive energy levels.

Flat ($\alpha=1/2$)		Cube ($\alpha=1$)		Square column ($\alpha=2$)	
This paper	Ref. 1	This paper	Ref. 1	This paper	Ref. 1
2	2	2	2	2	2
6	6	8	8	4	4
8	8	14	14	6	8
12	*12*	20	*16*	10	14
16	14	22	28	*16*	*18*
18	22	34	34	20	20
26	*24*	40	40	*24*	*26*
28	30	46	46	30	28
34	34			36	*32*
38	38			42	36
46	42			46	40
	46				44
					48

[1] W. F. Libby, J. Chem. Phys. **46**, 399 (1967).

Mechanisms of Vibrational Relaxation

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Vibrational relaxation of diatomic molecules has recently been discussed theoretically.[1] We should like to discuss and clarify the mechanisms considered in that work.

The changes in vibrational state of a molecule arise from the interactions of the vibrational coordinate with all other degrees of freedom. The interaction usually considered[2] is the direct potential energy between the oscillator and the other molecules in the system. For simplicity, this direct potential interaction is usually linearized in the oscillator coordinate, so that the interaction becomes proportional to the force f_{int} exerted on the oscillator by the other molecules. This direct interaction was considered in Sec. II of Ref. 1.

A second force experienced by the oscillator is the centrifugal force due to the rotation of the molecule. When linearized in the vibrational coordinate, this force is

$$f_{\text{cent}}=2E_R/R_0, \tag{1}$$

where R_0 is the equilibrium interatomic distance in the molecule, and E_R is the rotational kinetic energy.[3] This contribution has usually been ignored in treating vibrational relaxation. It is just this rotational contribution which was evaluated in Secs. V and VI,[1] and compared in order of magnitude with measurements of vibrational relaxation in Sec. VII.

In general one must include both the intermolecular force f_{int}, and the centrifugal force f_{cent} contributions. Then the total rate of relaxation, calculated as in Ref. 1, becomes

$$W_{n\to n-1}=\frac{nR_0^2}{2I\hbar\omega_0}\int_{-\infty}^{\infty}dt\,\exp(-i\omega_0 t)\times\langle[f_{\text{int}}(0)+f_{\text{cent}}(0)][f_{\text{int}}(t)+f_{\text{cent}}(t)]\rangle, \tag{2}$$

where I is the moment of inertia and ω_0 is the oscillator frequency. The calculation of the rotational

contribution made in Ref. 1 indicates that these centrifugal forces may make a significant contribution to the relaxation process, and may sometimes be the dominant mechanism. Note that Eq. (2) also contains interference terms between rotational and potential contributions, which have never been evaluated. A complete analysis should include estimates of these cross effects, and the rotational coupling, in addition to the potential contribution which is usually considered.

As an indication of the order of magnitude of these contributions to the vibrational relaxation, it is important to note that the rotational contribution alone, as estimated in Ref. 1, gives theoretical vibrational transition rates averaging about an order of magnitude smaller than experimental values. This may be seen in Fig. 1 of Ref. 1, in which the best theoretical estimate is the curve marked $\omega_0\tau_c=4$, while the experimental points tend to scatter about one order of magnitude lower in Z_{vib} (i.e., an order of magnitude larger in $W \propto Z_{\text{vib}}^{-1}$). Thus one would conclude from this comparison that the contribution of rotation–vibration coupling to vibrational relaxation is probably typically about an order of magnitude smaller than the direct potential interactions.

[1] B. J. Berne, J. Jortner, and R. Gordon, J. Chem. Phys. **47**, 1600 (1967).

[2] See, for example, K. F. Hertzfeld and T. A. Litovitz, *Absorption and Dispersion of Ultrasonic Waves* (Academic Press Inc., New York, 1959).

[3] The opposite sign is given for f_{cent} in Ref. 1, Eq. (V.3), because there the centrifugal force was evaluated from the force, of equal magnitude but *opposite sign*, which would be required to keep the oscillator rotating rigidly.

Errata

Erratum: Calculations on the Tetramethyl-*p*-phenylenediamine System

[J. Chem. Phys. **47**, 391 (1967)]

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In Fig. 1 the x and y axes of the TMPD system should be interchanged.

Erratum: Resonance Absorption of *p*-Benzosemiquinone in the Zeeman Region

[J. Chem. Phys. **47**, 5839 (1967)]

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There is a misprint in the above paper. Parts III of Tables VII and VIII should be interchanged.