Spectra and Structure of Crystalline Cyclopropane and Cyclopropane-D_6

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In a recent paper, Bates, Sands, and Smith[1] (hereafter BSS) report infrared spectra of crystalline films of cyclo-C_3H_6 and -C_3D_6 which differ in minor respects from our own.[2] In reply to their comments, we wish to make the following statements:

(1) Our cyclopropane crystal CH_2 stretching frequencies of 3086, 3072, and 3008 cm^{-1} were obtained on two different spectrometers, using different calibrations, which gave results agreeing within less than 1 cm^{-1}. The resulting gas–crystal frequency shifts of $\sim$15 cm^{-1} are normal with our data, which in fact agree well with the low-resolution prism frequencies of 3073 (components unresolved) and 3004 cm^{-1} of Brecher et al.[3] The frequencies quoted by BSS are consistently lower than ours by 12 cm^{-1} and lead to gas-crystal frequency shifts of almost 30 cm^{-1}.

(2) BSS have omitted to mention the most important difference between our data and theirs, *viz.*, our assignment of $\nu_4(a_1'')$ in cyclo-C_3D_6 to a very sharp line at 804.6 cm^{-1}, compared with their assignment to the band at 839 cm^{-1}. This latter assignment introduces a very serious discrepancy in the product-rule ratio in the a_1'' species (observed, 1.346; theoretical, 1.414) which BSS apparently did not test. The band at 839 cm^{-1} we assign to cyclo-C_3D_5H impurity, together with a band of similar peak height at 639.4 cm^{-1}, also unobserved by BSS. The correctness of this assignment is established by the force-field calculations of Duncan and Burns[4] which predict cyclo-C_3D_5H impurity bands at 834 and 640 cm^{-1}.

(3) Our observation of $\nu_{14}(e'')$ of cyclo-C_3D_6 in isotopic solid solution (not observed by BSS) as a single peak at 534.5 cm^{-1} is in good agreement with the Raman liquid frequency of 528 cm^{-1} and lies between our pure crystal bands at 530.3 and 540.1 cm^{-1} in the normal manner. See Fig. 1. The crystal frequencies of BSS imply an upward gas–crystal frequency shift of 20 cm^{-1}, which seems very large.

Our reaction to the published spectra of BSS is that they were obtained with an *actual* spectral slitwidth rather greater than 1 cm^{-1} on a spectrometer whose unconventional design may lead to complications due to incomplete filtering out of undesired orders of the grating.

As indicated by our note added in proof, we accept the alterations in assignments of the almost coincident absorptions ν_3 and ν_{13} in the crystal spectrum of cyclo-C_3H_6 made necessary by the work of Brecher et al.[3]
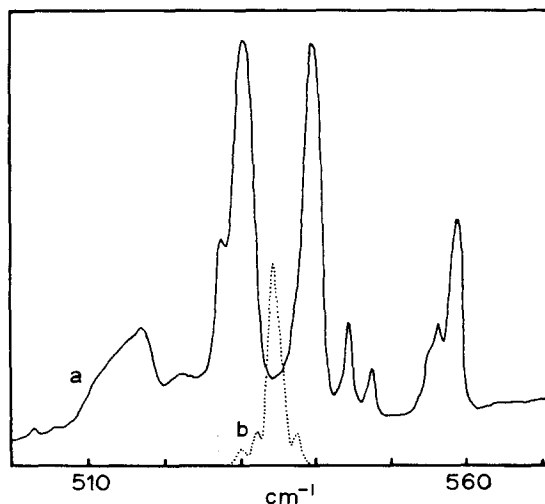

Fig. 1. Infrared spectra of crystalline films of cyclopropane-D_6 at 78°K, 570–500 cm^{-1}: (a), C_3D_6 (50 squirts of vapor); (b), 10% C_3D_6 in C_3H_6 (60 squirts of vapor).

We also agree that the assignments of the crystal frequencies 1433.9, 1431.8, and 1420.6 cm^{-1} to ν_9, and 1445.7 cm^{-1} to ν_2 in cyclo-C_3H_6 seem unavoidable at present.

[1] J. B. Bates, D. E. Sands, and W. H. Smith, J. Chem. Phys. 51, 105 (1969).
[2] J. L. Duncan and D. C. McKean, J. Mol. Spectry. 27, 117 (1968).
[3] C. Brecher, E. Krikorian, J. Blanc, and R. S. Halford, J. Chem. Phys. 35, 1097 (1961).
[4] J. L. Duncan and G. R. Burns, J. Mol. Spectry. 30, 253 (1969).

Errata

Erratum: On the Theory of Chemiluminescent Electron-Transfer Reactions

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The curve drawn in Fig. 1(c) of the above article indicates the "reaction path" leading to formation of ground state products in a highly exothermic electron transfer. The adiabatic curves are given instead[1,2] by Fig. 1. Thereby, the transition from the lower segment of the R (reactants') curve to that of this electronically unexcited P (products') curve is nonadiabatic. Thus, the argument that the rate constant for the case of
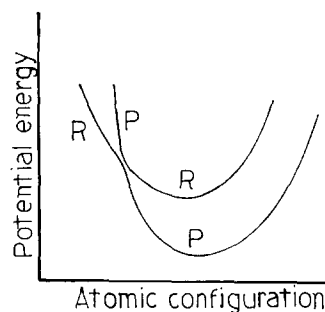
FIG. 1. Profile of potential-energy surface of reactants (R) and that of products (P) plotted versus configuration of all the atoms in the system, for the case of very negative ΔF°.

Fig. 1(c) for formation of the electronic ground state of products is small, made there on energetic grounds, is now further strengthened: That rate constant is decreased by a transition probability factor[3] for non-adiabatic reactions. The remaining discussion is unchanged.

[1] In comparison, see, R. A. Marcus, Discussions Faraday Soc. **45**, 7 (1968), Footnote 1. I am indebted to Dr. W. D. Weir for his helpful remarks.

[2] A similar remark applies to the corresponding curves in G. Hoytink, Discussions Faraday Soc. **45**, 14 (1968), and D. M. Hercules, Accounts Chem. Res. **2**, 301 (1969).

[3] For example, see, S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Co., Inc., New York, 1941), p. 149; E. E. Nikitin, in *Chemische Elementarprozesse*, H. Hartmann, Ed. (Springer–Verlag, New York, 1968), pp. 43–77.

Erratum: Self-Diffusion Coefficients and Rotational Correlation Times in Polar Liquids

[J. Chem. Phys. **49**, 5416 (1968)]

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In liquid HF, only exponential recovery of the proton longitudinal magnetization I_Z after 180° pulse was observed. The theory of Solomon and Bloembergen[1] predicts nonexponential recovery of I_Z as follows:

$$I_Z = I_0 \{ \exp(-t/T_1) + \exp(-t/D_1) \},$$

where

$$T_1^{-1} = \tfrac{3}{2}\delta,$$

$$D_1^{-1} = \tfrac{1}{2}\delta + (A^2/\hbar^2)[\tau_e/(1+\Delta\omega^2\tau_e^2)],$$

$\delta = \hbar^2\gamma_H^2\gamma_F^2\tau_2/R^6$, A/h is the proton–fluorine coupling constant, τ_e is the proton exchange time and $\Delta\omega = \omega_H - \omega_F$. Hence in our experiments

$$(A^2/\hbar^2)[\tau_e/(1+\Delta\omega^2\tau_e^2)] \approx \delta$$

which yields $\tau_e \approx 5 \times 10^{-8}$ sec at 298°K to be consistent with the measured value of T_2. We put

$$1/T_1 = \delta,$$

i.e., the average value of $1/T_1$ and $1/D_1$ in the absence of exchange. Actually we should have $T_1^{-1} = \tfrac{3}{2}\delta$. This results in a measured τ_2 that is $\tfrac{2}{3}$ of the value of τ_2 given in Table II for HF.

[1] I. Solomon and N. Bloembergen, J. Chem. Phys. **25**, 261 (1956).

Erratum: Molecular Constants of Lithium Hydrides by the Molecular-Beam Electric Resonance Method

[J. Chem. Phys. **50**, 1899 (1969)]

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All the c_3 (spin–spin interaction) values in Table I should be multiplied by 25, including the error estimates. In the computer printout they appeared as $c_3/5$ and in converting them to c_3 values this mistake occurred. They are in agreement with calculated values $(c_3 = g_1 g_2 u_N^2 \langle 1/r^3 \rangle_{Av})$ and are represented in Table I to show this. I thank Dr. L. Peter Gold for informing me.