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The weak rare-gas-induced absorption in the null gap of the HCl fundamental band, observed by Rank, Wiggins, and their co-workers,3 has been analyzed by Bratoz and Martin.² They ascribe the absorption to the presence of weakly bound HCl-rare-gas molecules. The spectra appear to result from the existence of an attractive van der Waals potential which accounts for the binding, and a weak $P_1(\cos\theta)$ force operating between HCl and the rare-gas atom within the complex. The $P_1(\cos\theta)$ force appears to be roughly equal to that associated with quadrupole-induced-dipole type forces acting alone.¹⁷ Hence, it can be concluded that the $P_1(\cos\theta)$ forces are relatively very weak near the HClrare-gas van der Waals minimum. This is a reasonable result, in view of the fact that, if the long-range attractive and short-range repulsive forces were to act at the same effective center in HCl (which is not obviously the case, however), the $P_1(\cos\theta)$ -dependent interaction would by definition be zero at the equilibrium separation.

In analyzing the spectra of HCl molecules trapped in solid Ar lattices, Friedmann and Kimel⁴ have found that certain features of the absorption spectrum can be explained on the assumption of a $P_1(\cos\theta)$ -dependent potential. Their analysis showed that the interaction effectively acts at a point removed a distance 0.09 Å from the center of mass in HCl. Here, again, short-range forces are important, a fact that prevents one from unambiguously associating the above value for d with that characteristic of the long-range forces alone. Notwithstanding this difficulty, the theoretical value of dderived in this paper seems generally compatible with the latter measurement.

Finally, the author⁵ has analyzed the He- and Arinduced absorption in the HCl fundamental-band Qbranch at high pressures, as has been observed by Vodar, Vu, Coulon, and others.¹⁸ Generally good agreement between theoretical predictions based on the value for d obtained in this paper, and experimental results has been achieved. However, the results are rather strongly dependent on ones assumptions about the behavior of the $P_1(\cos\theta)$ interactions at short range, which isn't known as yet. Consequently, the comparison, here, does not really afford a good quantitative test of the magnitude of d.

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Microwave Spectrum, Dipole Moment, and Ring-Puckering Vibration of Vinylene Carbonate*

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The microwave spectrum of vinylene carbonate has been studied in the frequency region between 12 000 and 26 500 Mc/sec. Rotational constants and moments of inertia have been derived for the vibrational ground state and for the first three excited states of the ring-puckering vibrational mode. The molecule is planar, with no barrier at the planar configuration in the ring-puckering potential function. Measured intensities of the vibrational satellites are fitted well by a purely quadratic potential function. The dipole moment, which lies exclusively along the a axis, is 4.57 ± 0.05 D.

MOLECULE containing a four-membered ring A which is planar or nearly planar has one normal mode of vibration in which the ring atoms move perpendicularly to the plane of the ring. A five-membered ring has two ring-puckering modes of this type which may or may not interact to produce a pseudorotation such as has been reported in cyclopentane¹ If the ring contains a double bond, resistance to torsion around

the double bond is so much greater than for torsion around the single bonds that interaction should not occur and the lowest-frequency vibrational mode should be the simple ring-puckering vibration involving torsion around the single bonds.²

The nature of the potential function governing the ring-puckering vibration is of considerable interest. For a strain-free ring with no torsional barrier, the potential function must be quartic for small displacements from the plane of the ring.³ A barrier to torsion about the single bonds in the ring introduces a quadratic term

² G. W. Rathjens, Jr., J. Chem. Phys. 36, 2401 (1962) ³ R. P. Bell, Proc. Roy. Soc. (London) A183, 328 (1945).

¹⁷ For Ar-HCl and Xe-HCl at equilibrium separation, the quadrupole-induced dipole coefficients for the $P_1(\cos\theta)$ inter-actions are 7.2 and 8.9 cm⁻¹ theoretically, to be compared with the values ± 7 and ± 14 cm⁻¹ suggested by Bratož and Martin in their analysis.

¹⁸ See, for example, B. Vodar and H. Vu, J. Quant. Spectry. Radiative Transfer **3**, 397 (1963); H. Vu, J. Rech. CNRS **11**, 313 (1960); R. Coulon, *ibid.* **9**, 305 (1958). Other references are cited in these papers.

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College of Technology, Beaumont, Texas. ¹ J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, J. Am. Chem. Soc. 69, 2483 (1947).

Transition	v = 0		v = 1		v=2		v=3		v = 4
	Observed frequencies	veale ^{-v} obs	Observed frequencies	vcale vobs	Observed frequencies	veale vobs	Observed frequencies	v _{calc} -v _{obs}	Observed frequencies
$1_{11} \rightarrow 2_{12}$	12 863.22	-0.02		•••	12 895.89	-0.04	•••	•••	•••
$1_{01} \rightarrow 2_{02}$	13 944.63	-0.03	13 958.43	-0.03	•••	• • •	13 986.34	-0.01	•••
$1_{10} \rightarrow 2_{11}$	15 456.43	+0.01	15 470.55	0.00	15 484.76	+0.01	• • •	•••	•••
$2_{12} \rightarrow 3_{13}$	19 169.87	-0.03	19 193.49	-0.03	19 217.34	-0.01	19 241.26	+0.03	19 265.48
2 ₀₂ →3 ₀₃	20 415.43	-0.01	20 433.42	0.00	20 451.58	0.00	20 469.93	+0.02	•••
$2_{21} \rightarrow 3_{22}$	21 239.76	-0.03	21 262.55	-0.06	21 285.45	+0.01	21 308.47	+0.02	•••
$2_{20} \rightarrow 3_{21}$	•••	•••	22 091.48	+0.06	•••	• • •	•••	•••	•••
$2_{11} \rightarrow 3_{12}$	23 036.96	-0.04	23 057.10	+0.01	23 077.40	0.02	23 097.73	-0.02	23 118.59
$3_{13} \rightarrow 4_{14}$	25 355.55	+0.11	25 386.14	+0.01	25 416.94	+0.03	25 447.98	-0.04	25 478.88
3 ₀₃ -→4 ₀₄	•••	•••	26 471.74	+0.02	•••	•••	•••	•••	•••
5 ₁₅ →5 ₁₄	18 845.44	-2.40	•••	•••	•••	•••	•••	•••	•••
6 ₁₈ →6 ₁₅	25 518. 04	-2.33	•••	•••	•••	•••	•••	•••	•••
8 ₂₇ →8 ₂₆	23 295.65	-0.99	23 325.59	-1.24	•••	•••	•••	•••	•••

TABLE I. Rotational transitions of vinylene carbonate (in megacycles per second).

into the potential function as does the angle-deformation strain energy if the valence angles are already strained in the planar configuration.⁴ A mixed quadraticquartic potential function has been observed for such molecules as trimethylene oxide,⁴ trimethylene sulfide,⁵ and diazomethane,⁶ while a purely quadratic function explains within experimental error the observed energy levels in cyclobutyl chloride,⁷ cyclobutyl fluoride,⁷ and propiolactone.⁸ It has been pointed out⁹ that dominance of the quartic term will be observed if the ring strain in the planar configuration is canceled by the torsional forces about the single bonds of the ring skeleton and that the quartic term should be small if such cancellation of opposing force fields does not occur.

Vinylene carbonate



contains a five-membered ring for which pseudorotation would not be expected and for which the lowest-frequency vibrational mode should be a simple ringpuckering motion. A previous microwave investigation¹⁰ of the ground vibrational state has established that the molecule is planar and given values for the rotational constants of the ground state and the dipole moment. The present study was undertaken to examine the nature of the ring-puckering vibration.

EXPERIMENTAL

The apparatus used in this study was a conventional Stark-effect microwave spectrometer with 100 kc/sec modulation and a 10-ft sample cell made of X-band waveguide. Vinylene carbonate was prepared from ethylene carbonate by photochemical chlorination to give the mono-chloro derivative, followed by dehydrochlorination with triethylamine to yield the desired product. The sample was purified by fractional distillation and was shown to have satisfactory purity by mass spectrometry.

MICROWAVE SPECTRUM

Since vinylene carbonate is a planar molecule with the dipole moment along the a axis, only a-type transitions can be observed The vibrational satellite system, arising from rotational transitions of molecules in excited vibrational states, was relatively sparse with one clearly distinguishable family of lines of appreciable intensity accompanying each vibrational ground-state transition. The vibrational mode of lowest frequency in vinylene carbonate should be the out-of-plane ring puckering vibration, so the observed family of satellite lines was tentatively assigned to such a motion. The measured frequencies of the observed lines are shown in Table I. The rotational constants calculated from these measurements are given in Table II.

The rotational constants were calculated by a leastsquares fitting of all of the observed R-branch transitions omitting the higher-J, Q-branch lines for which the effects of centrifugal distortion would be expected to be more prominent. As can be seen from Table I, the

⁴S. I. Chan, J. Zinn, and W. D. Gwinn, J. Chem. Phys. 34, 1319 (1961).

⁶ D. O. Harris, H. W. Harrington, and W. D. Gwinn, paper presented at Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 14-18 June 1965.

⁶C. B. Moore and G. C. Pimentel, J. Chem. Phys. 40, 1529 (1964).

⁷ H. Kim and W. D. Gwinn, Bull. Am. Phys. Soc. 10, 491 (1965).

⁸ D. W. Boone, C. O. Britt, and J. E. Boggs, J. Chem. Phys. 43, 1190 (1965).
⁹ S. I. Chan, D. Stelman, and L. E. Thompson, J. Chem. Phys.

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 2828 (1964).
 ¹⁰ G. R. Slayton, J. W. Simmons, and J. H. Goldstein, J. Chem.

¹⁰ G. R. Slayton, J. W. Simmons, and J. H. Goldstein, J. Chem Phys. **22**, 1678 (1954).

v	A	В	С
0	9344.9	4188.265	2891.645
1	9301.8	4191.525	2895.970
2	9258.4	4194.810	2900.345
3	9216.7	4198.095	2904.735

TABLE II. Calculated rotational constants (in megacycles per second).

agreement between the experimental and calculated frequencies is quite good. Since only *a*-type transitions are observed, the least moment of inertia can be known to less accuracy than the other two. The fit between the calculated and observed frequencies becomes worse if A is changed by ± 0.5 Mc/sec or if B or C is changed by ± 0.005 Mc/sec. This precision should apply in comparisons made between the values obtained for the different vibrational states, but the absolute accuracy is probably less by a factor of 2 to 4. Three measured transitions are listed in Table I for the fourth excited vibrational state, but the data are too limited to allow calculation of rotational constants with sufficient accuracy to permit meaningful comparison with the results for the lower states.

RING-PUCKERING VIBRATION

The rotational constants listed in Table II can be used to calculate the principal moments of inertia of vinylene carbonate, which are listed in Table III. The inertia defect, $\Delta = I_c - I_a - I_b$, is so nearly zero in the ground state that the planar structure is confirmed.

The identification of the series of excited-state transitions listed in Table I with the ring-puckering vibration is based first on the observation that no other excitedstate lines are found with comparable intensity. By comparison with results for similar molecules, the outof-plane ring mode would be expected to be the lowest vibrational fundamental so that the excited states would be more highly populated and the corresponding rotational transitions would be more intense than for other modes. The assignment is supported by the variation of the inertia defect with vibrational state shown in Table III. If an out-of-plane vibration is sufficiently lower in frequency than other modes with which it can interact, as appears to be the case with vinylene carbonate, it has been shown¹¹ that the inertia defect becomes progressively more negative as the out-of-plane mode is excited to higher states.

Certain molecules which are planar in the ground vibrational state have been found to have a small barrier at the planar configuration so that the equilibrium configuration would be nonplanar In such a case, the vibrational energy levels would be paired to some extent, with a consequent alternating variation in the differences between the rotational constants for adjacent vibrational states.^{4,12} The rotational constants listed in Table II show no evidence of such behavior, so the vibrational potential function appears to have a single minimum at the planar configuration.

Relative intensity measurements were made on the excited-state lines of certain of the rotational transitions, taking special precautions to maintain constant power at the detector and to eliminate effects due to reflections and system nonlinearity.13 Since vinylene carbonate has C_{2v} symmetry and two hydrogen atoms that are interchanged by rotation of 180° around the symmetry axis, the ratio of the number of symmetric spin functions to antisymmetric spin functions is 3:1. The electronic and vibrational ground states are symmetric and Fermi-Dirac statistics are obeyed, so the antisymmetric rotational states (those with K_{-1} odd) are more populated by the ratio of 3:1 than the symmetric rotational states. For the excited vibrational states, the vibrational wavefunction alternates in symmetry so that the nuclear-spin factor also alternates. Thus for the 2_{11} level, the nuclear-spin factor is 3, 1, 3, 1, \cdots for $v=0, 1, 2, 3, \cdots$ while for the 2_{02} level, the spin factor is 1, 3, 1, 3, \cdots for the same vibrational states.

The nuclear-spin statistics correction was applied to the measured relative intensities, and the results are shown in Table IV. The value listed for each transition is the average of several independent measurements. The average values listed in the table are obtained by considering all of the individual measurements separately and the uncertainty is the standard deviation of the mean. Using the Boltzmann distribution of population, the energies of the successive vibrational states were calculated and are shown in Table IV. The uncertainty of 20 cm⁻¹ is appreciably larger than would be calculated by a statistical analysis of the data and is intended as an estimate of the absolute accuracy of the result including various possible sources of constant error.

If there were an energy barrier in the potential function at the planar configuration, the resulting pairing of the vibrational energy levels should appear in

TABLE III. Moments of inertia and inertia defect in atomic mass units square angstrom.^a

v	I_a	I _b	I _c	Δ
0	54.081	120.6650	174.7714	+0.025
1	54.331	120.5712	174.5104	-0.392
2	54.586	120.4767	174.2472	-0.816
3	54.833	120.3824	173.9838	1.231

^a Conversion factor: I_a =5.05377×10⁵/A, corresponding to ¹²C=12 atomic weight scale.

 ¹² S. I. Chan, J. Zinn, J. Fernandez, and W. D. Gwinn, J. Chem. Phys. 33, 1643 (1960).
 ¹³ A. S. Esbitt and E. B. Wilson, Jr., Rev. Sci. Instr. 34, 901

¹³ A. S. Esbitt and E. B. Wilson, Jr., Rev. Sci. Instr. **34**, 901 (1963).

¹¹ K. Kuchitsu, T. Oka, and Y. Morino, J. Mol. Spectry. 15, 51 (1965).

	v = 0	v = 1	v=2	v = 3	v = 4
$2_{11} \rightarrow 3_{12}$	1.000	0.308	0.094	•••	•••
$2_{12} \rightarrow 3_{13}$	1.000	0.301	0.095	0.034	0.0096
$2_{21} \rightarrow 3_{22}$	1.000	0.311	0.096	0.033	•••
$2_{02} \rightarrow 3_{03}$	1.000	0.324	0.101	0.029	• • •
$3_{13} \rightarrow 4_{14}$	1.000	0.285	0.094	0.032	0.0101
Average	1.000	0.307 ± 0.006	0.096 ± 0.002	0.032 ± 0.001	0.0099 ± 0.0003
$\overline{\nu}(\mathrm{cm}^{-1})$	0	250 ± 20	490 ± 20	720 ± 20	960 ± 20

TABLE IV. Intensities^a of excited-state transitions relative to the ground state and the corresponding vibrational energies.

⁸ Corrected for nuclear-spin statistics.

the relative intensity data. Since no such variation is evident within the rather limited accuracy of the meassurements, further confirmation of the absence of a barrier is obtained.

Having established that the potential function for the ring-puckering motion has a single minimum, we may next examine the data to determine the dependence of the energy on vibrational amplitude. For a purely quadratic potential function, the vibrational energy levels are evenly spaced. A quartic term causes the energy levels to diverge with increasing values of v. There is no evidence in vinylene carbonate for the latter behavior, and the vibrational energy levels can be represented by $E_v = (244 \pm 4) (v + \frac{1}{2})$ cm⁻¹, corresponding to a purely quadratic potential function. The 4 cm⁻¹ uncertainty in this expression represents internal consistency of the measurements and not absolute accuracy.

A quadratic term in the potential function that completely overwhelms any quartic term can be interpreted either as indicative of a large ring strain at the planar configuration or of a large barrier to torsion around the ring bonds. The former interpretation seems

TABLE V. Dipole moment of vinylene carbonate.

Transition	М	v = 0	v = 1	v = 2
$2_{11} \rightarrow 3_{19}$	0	4.52	•••	
	1	4.62	4,64	4.56
	2	4.46	•••	•••
3 ₁₃ →4 ₁₄	0	4.62	•••	•••
	1	4.59	•••	4.58
	2	4.53	4.60	4.50
Average		$4.56 {\pm} 0.05$	4.62 ± 0.02	$4.55{\pm}0.03$

more probable, but a quantitative treatment does not seem practicable without more reliable data on the structural parameters of the ring.

DIPOLE MOMENT

Although the dipole moment of vinylene carbonate has been measured previously,10 the large value of 4.51 ± 0.05 D obtained made it seem worthwhile to check the measurement. The spectrometer was calibrated using the $J=1\rightarrow 2$ transition of OCS, taking the dipole moment of OCS of 0.7124 D.14 The Stark shifts of selected transitions in the ground and first two excited vibrational states were measured and found to be of second order, as expected. From these measurements, the dipole moment, which lies exclusively along the *a* axis, was calculated. The results are shown in Table V. Each value shown was calculated from the least-squares slope of a plot of frequency shift against the square of the applied electric field strength. The average of all of the measurements is 4.57 D with a standard deviation of 0.05 D. This result agrees within experimental error with the previously published value,¹⁰ and any variation of dipole mement with vibrational state is below the accuracy of the present measurements.

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¹⁴S. A. Marshall and J. Weber, Phys. Rev. 105, 1502 (1957).