

# JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office. © Copyright 1974 by the American Chemical Society

VOLUME 96, NUMBER 18

SEPTEMBER 4, 1974

## Calculation of $\pi\pi^*$ Excited State Conformations and Vibronic Structure of Retinal and Related Molecules<sup>1</sup>

A. Warshel<sup>2</sup> and M. Karplus\*

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. Received October 29, 1973

**Abstract:** A semiempirical method for the evaluation of ground and  $\pi\pi^*$  excited state equilibrium conformations and vibrational spectra of conjugated molecules is applied to  $\beta$ -ionone and 11-*cis*- and *all-trans*-retinal. The minimum energy conformations and the harmonic vibrational frequencies for each potential surface are evaluated in the complete  $3n$ -dimensional space of the molecule. To examine the effect of large torsion of individual bonds, an "adiabatic" procedure is used for minimizing the molecular energy as a function of all coordinates other than the one of interest. From the vibrational analysis of the two electronic states involved, the relative vibronic intensities (Franck-Condon factors) for the  $\pi\pi^*$  transition of  $\beta$ -ionone and 11-*cis*- and *all-trans*-retinal are calculated. The modes with significant Franck-Condon factors are found to correspond in most cases with the active modes observed in resonance Raman experiments. The origin of the diffuse absorption spectrum in  $\beta$ -ionone and the retinal isomers and the source of the strong temperature dependence of the spectrum of 11-*cis*-retinal are examined by a series of model calculations.

The initial step in vertebrate vision is light absorption by 11-*cis*-retinal, the chromophore of the visual pigment rhodopsin.<sup>3</sup> This apparently causes photoisomerization of the 11-*cis* isomer to a species that is 11-*trans* and initiates further steps in the visual process. A detailed study of the properties of the excited states of retinal is the first step in an investigation of the photoisomerization reaction. Such a study requires a method which permits one to make reliable calculations of the equilibrium conformations of the relevant electronic surfaces and of their vibrational properties. Starting from these results, the vibronic coupling between the various electronic levels can be determined and a dynamic description of the photoisomerization can be developed.

We have previously described a semiempirical method for the treatment of the equilibrium conformations and vibrational spectra of the ground and excited states of conjugated molecules.<sup>4</sup> The results of such

calculations have been employed in the quantitative interpretation of the vibrational structure of electronic transitions of molecules such as ethylene, butadiene, cyclohexadiene, and  $\beta$ -ionone.<sup>5</sup> It has been demonstrated<sup>6</sup> that the method yields rather accurate equilibrium conformations and other properties of the ground state potential surface of various retinal isomers. In the present paper, we continue our study of the retinal isomers. We deal with the properties of the often-calculated  $\pi\pi^*$  excited singlet state and with the evaluation of the Franck-Condon factors for the transition to it from the ground state. In addition, we explore the effect of steric repulsion on the vibronic structure of the electronic transition. The relief of steric repulsion has been suggested as a qualitative explanation for the apparent red shift which appears upon cooling in the spectrum of 11-*cis*-retinal,<sup>7,8</sup> as well as of other sterically hindered molecules.<sup>9,10</sup> However, it has not been possible to examine quantitatively the dependence

(1) Supported in part by the National Science Foundation, the National Eye Institute and the Israel Academy of Sciences and Humanities.

(2) Department of Chemical Physics, Weizmann Institute, Rehovot, Israel.

(3) G. Wald, *Science*, **162**, 230 (1968); W. E. Abramson and S. E. Ostroy, *Progr. Biophys. Mol. Biol.*, **17**, 170 (1967); R. Hubbard and G. Wald in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1968.

(4) A. Warshel and M. Karplus, *J. Amer. Chem. Soc.*, **94**, 5612 (1972).

(5) A. Warshel and M. Karplus, *Chem. Phys. Lett.*, **17**, 7 (1972).

(6) R. Rowan, A. Warshel, B. Sykes, and M. Karplus, *Biochemistry*, **13**, 970 (1974); A. Warshel and M. Karplus, unpublished.

(7) G. Wald, *Nature (London)*, **184**, 640 (1959).

(8) W. Sperling and C. N. Rafferty, *Nature (London)*, **224**, 591 (1969).

(9) H. H. Jaffe and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," Wiley, London, 1962; "Steric Effect in Conjugated Systems," G. W. Gray, Ed., Butterworths, London, 1958.

(10) H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press, New York, N. Y., 1967.

of the vibronic structure on the steric repulsion; we make such an examination in this paper.

In section I the method used in the calculation of the excited state potential surface of  $\beta$ -ionone and 11-*cis*- and *all-trans*-retinal is outlined and the results obtained are described. The minimum energy geometry and an "adiabatic" torsional potential for certain significant bonds are presented. These potentials are compared with the corresponding ground state potentials, and the expected consequences of the differences in curvature and the location of the minimum are discussed. The calculations of vibronic intensities for the strongly allowed  $\pi\pi^*$  transition in retinal and  $\beta$ -ionone are presented in section II and reasons for the diffuseness of the observed spectra are considered. In section III, the temperature dependence of the spectrum of 11-*cis*-retinal is examined by model calculations. The conclusions are outlined in section IV.

### I. Excited State Potential Surface

Details of the method for the evaluation of potential surfaces of conjugated molecules have been given previously,<sup>4</sup> so that we mention here only a few essential points. To permit the rapid determination of the potential surface with simultaneous variation of all coordinates (*i.e.*, bond lengths, bond angles, and torsional angles), the  $\sigma$  and  $\pi$  electrons are assumed separable and the total potential energy  $V^N(\mathbf{r})$  is expressed as an analytic function of the molecular coordinates  $\mathbf{r}$  in the form

$$V^N(\mathbf{r}) = V_\sigma(\mathbf{r}) + V_\pi^0(\mathbf{r}) + \Delta V_\pi^N(\mathbf{r}) \quad (1)$$

where  $V_\sigma(\mathbf{r}) + V_\pi^0(\mathbf{r})$  is the sum of  $\sigma$ - and  $\pi$ -electron energies for the ground state and  $\Delta V_\pi^N(\mathbf{r})$  is the  $\pi$ -electron excitation energy. The function  $V_\sigma(r)$  is an empirical expression of the type used in potential surface calculations for saturated hydrocarbons.<sup>11</sup> The  $\pi$ -electron contribution is based on the SCF-LCAO-MO-CI method of the Pariser-Parr-Pople type (corrected for nearest neighbour overlap). To obtain the derivatives of the energy with respect to the coordinates,  $V_\sigma(\mathbf{r})$  is differentiated directly and  $V_\pi^0(\mathbf{r})$  and  $\Delta V_\pi^N(\mathbf{r})$  are approximated for a point  $\mathbf{r}$  in the neighborhood of a point  $\mathbf{r}^s$ ; *e.g.*,  $\Delta V_\pi^N(\mathbf{r})$  is written

$$\Delta V_\pi^N(\mathbf{r}) = \sum_\nu R_{\nu\nu} W(\mathbf{r}^s)^\lambda W(\mathbf{r}) + \sum_{\nu>\mu} R_{\nu\nu} \gamma(\mathbf{r}^s)^\lambda \gamma_{\nu\nu}(\mathbf{r}) + \sum_{\nu>\mu} R_{\nu\mu} \beta(\mathbf{r}^s)^\lambda \beta_{\nu\mu}(\mathbf{r}) + \sum_{\nu>\mu} R_{\nu\mu} \gamma(\mathbf{r}^s)^\lambda \gamma_{\nu\mu}(\mathbf{r}) \quad (2)$$

where the  $R$  coefficients are obtained from the eigenvectors of the Fock and CI matrices at  $\mathbf{r}^s$  and the  $^\lambda W(\mathbf{r})$ ,  $^\lambda \beta_{\nu\mu}(\mathbf{r})$ , and  $^\lambda \gamma_{\nu\mu}(\mathbf{r})$  are semiempirical  $\pi$ -electron integrals in the Lowdin representation<sup>4</sup> evaluated at  $\mathbf{r}$ . The resulting approximate analytic expression for  $V^N(\mathbf{r})$  allows one to apply efficient minimization techniques to find the minimum of the multidimensional potential surface. At the calculated minimum, the vibrational frequencies are determined from the analytic second derivatives of the molecular potential.

In applying the method to the potential surfaces of  $\beta$ -ionone and certain retinal isomers, the parameters for carbon and hydrogen given in ref 4 were employed. The presence of the aldehyde oxygen required additional  $\sigma$ - and  $\pi$ -electron parameters; they are listed in Table I in notation corresponding to that of ref 4. Only singly

(11) S. Lifson and A. Warshel, *J. Chem. Phys.*, **49**, 5116 (1968).

Table I. Parameters for the C=O Bond<sup>a</sup>

Parameter	Value	Parameter	Value
$\pi$ Integrals			
$\beta_0$	-2.05 eV	$I - A$ of O	15.3 eV
$\mu_\beta$	2.035 $\text{\AA}^{-1}$	$G_0$	10.8 eV
$b_0^1$	1.30 $\text{\AA}$	$G_s$	
$W_{sp}^0$ of O	-17.7 eV	$\mu_\gamma$	0.232 $\text{\AA}^{-1}$
$\beta_0^1$ of O			
$\sigma$ Functions			
$D_e$	85 kcal	$\alpha$	1.756 $\text{\AA}^{-1}$
$b_0$	1.466 $\text{\AA}$		

<sup>a</sup> The notation is as in ref 4.

excited  $\pi$ -electron configurations were included in the CI matrix, since they make the dominant contribution to the excited state considered here; doubly excited configurations would have to be included for twisting to large angles (as in photoisomerization) and for certain other polyene excited states.<sup>12</sup>

The calculated minimum energy conformations of the strongly allowed  $\pi\pi^*$  excited singlet of the *all-trans* isomer and of the 11-*cis*,12-*s-cis* rotamer of retinal are given in Tables II and III, respectively; corresponding results for

Table II. Calculated Excited State Equilibrium Conformation of *all-trans*-Retinal<sup>a,b</sup>

Bond	Value	$\Delta^c$
5,6	1.373	0.01
6,7	1.477	-0.02
7,8	1.382	0.03
8,9	1.435	-0.04
9,10	1.414	0.05
10,11	1.410	-0.05
11,12	1.411	0.05
12,13	1.426	-0.05
13,14	1.406	0.04
14,15	1.428	-0.02
Bond angle		
5,6,7	122.4	0.8
6,7,8	124.3	0.8
7,8,9	124.1	0.0
8,9,10	117.4	-0.2
9,10,11	125.6	-0.3
10,11,12	120.3	-0.2
11,12,13	125.4	-0.2
12,13,14	117.7	0.0
13,14,15	124.6	-0.3
Torsional angle <sup>d</sup>		
4,5,6,7	178	0
5,6,7,8	-41	8
6,7,8,9	-174	1
7,8,9,10	165	-2
8,9,10,11	-174	5
9,10,11,12	171	-2
10,11,12,13	-175	4
11,12,13,14	172	0
12,13,14,15	-178	2

<sup>a</sup> Bond lengths in  $\text{\AA}$ , angles in degrees; for the numbering scheme, see Figure 1. <sup>b</sup> The customary designation "all-trans" is used for this molecule, although it has a distorted *s-cis* conformation around the 6-7 bond. <sup>c</sup>  $\Delta$  is the difference between excited state and ground state equilibrium internal coordinates ( $\Delta = S_{\text{excited}} - S_{\text{ground}}$ ). <sup>d</sup> The convention for the torsional angles is that  $0^\circ$  corresponds to *cis* or *s-cis* and for the angle  $i - 1, i, i + 1, i + 2$  in looking from  $i + 1$  to  $i$  a counterclockwise rotation of the  $i + 1, i + 2$  bond is positive.

$\beta$ -ionone are given in Table IV. The torsional angle convention used is given in a footnote of Table II.

(12) K. Schulten and M. Karplus, *Chem. Phys. Lett.*, **14**, 305 (1972).

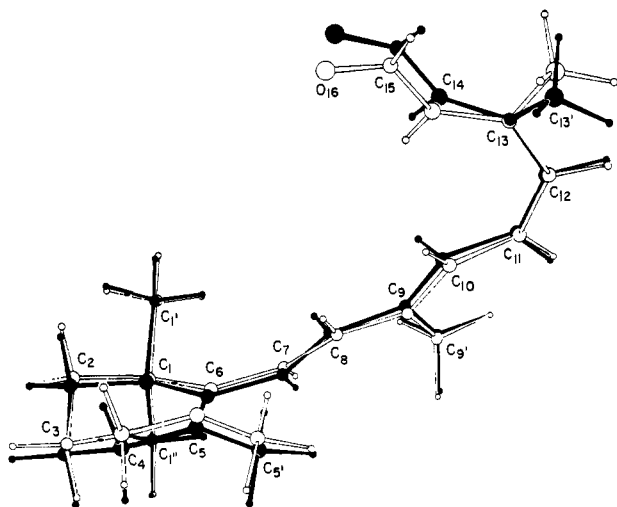


Figure 1. The equilibrium conformations of the ground state and the  $\pi\pi^*$  singlet of 11-*cis*,12-*s-cis*-retinal: (●) ground state, (○) excited state.

Table III. Calculated Excited State Equilibrium Conformation of 11-*cis*,12-*s-cis*-Retinal<sup>a</sup>

Bond	Value	$\Delta$
5,6	1.375	0.01
6,7	1.473	-0.02
7,8	1.384	0.03
8,9	1.433	-0.05
9,10	1.413	0.05
10,11	1.408	-0.06
11,12	1.417	0.05
12,13	1.428	-0.04
13,14	1.407	0.04
14,15	1.426	-0.02
Bond angle		
5,6,7	122.1	0.2
6,7,8	124.1	0.4
7,8,9	125.1	0.3
9,10,11	126.7	0.9
10,11,12	124.1	-1.7
11,12,13	127.1	-1.5
12,13,14	122.2	-0.2
13,14,15	125.1	0.4
Torsional angle		
4,5,6,7	177	-1
5,6,7,8	-38	7
6,7,8,9	-176	2
7,8,9,10	168	-6
8,9,10,11	183	5
9,10,11,12	168	-1
10,11,12,13	-20	-10
11,12,13,14	-16	12
12,13,14,15	177	-3

<sup>a</sup> Notation as is Table II.

Although all hydrogen and methyl group coordinates were calculated, only the conjugated chain bond lengths, bond angles, and torsional angles are listed for simplicity. Since the main factor which determines the vibronic structure of the electronic transition is the difference in the equilibrium coordinates between the ground and excited states, the "origin shifts,"  $\Delta$ , are included in the tables; the ground state geometries are given in ref 6. To illustrate these results, the equilibrium conformations of the ground and excited state of the 11-*cis*, 12-*cis* rotamer of retinal are shown in Figure 1 and those for  $\beta$ -ionone in Figure 2. The representations of the two states of each molecule are

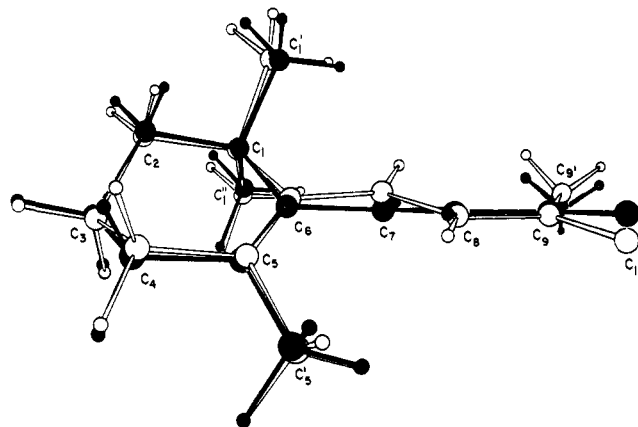


Figure 2. The equilibrium conformations of the ground state and the  $\pi\pi^*$  singlet of  $\beta$ -ionone: (●) ground state, (○) excited state.

Table IV. Calculated Excited State Equilibrium Conformation of  $\beta$ -Ionone<sup>a</sup>

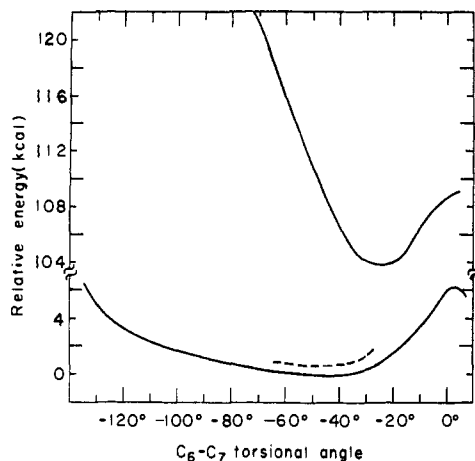
Bond	Value	$\Delta$
5,6	1.428	0.07
6,7	1.421	-0.08
7,8	1.437	0.08
8,9	1.415	-0.04
9,10	1.263	0.05
Bond angle		
5,6,7	122.5	0.0
6,7,8	125.0	0.2
7,8,9	122.9	-0.6
8,9,10	116.9	-1.2
Torsional angle		
4,5,6,7	168	-10
5,6,7,8	-20	20
6,7,8,9	175	7
8,9,10,11	179	0

<sup>a</sup> Notation as in Table II.

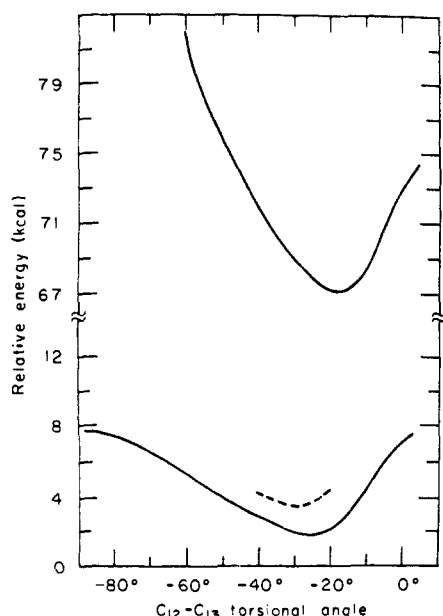
drawn so as to satisfy the Eckart condition;<sup>13</sup> that is, the vector of conformational change for the excited state relative to the ground state is given in terms of the  $3n - 6$  normal coordinates of the ground state without any contribution from rotational or translational modes. It is evident from the tables and figures that the calculated excited state conformations do not differ drastically from the corresponding ground state conformations. However, it is important to note that there are nonnegligible changes in almost all of the bond lengths, bond angles, and torsional angles. The calculated shift in certain torsional angles upon excitation, as a result of the change in the balance between steric repulsions and the  $\pi$ -electron energies, is most significant but does not exceed  $12^\circ$  in retinal and  $20^\circ$  in  $\beta$ -ionone. The carbon-carbon bond-length alterations on excitation of the retinals are, as expected, somewhat smaller than the corresponding changes in butadiene; in that molecule the bond lengths change by  $\pm 0.09 \text{ \AA}$  on excitation. It is also of interest to note that in the polyene chain of the retinals the central C-C bonds change more on excitation than those toward the ends. These results conform to the alteration of  $\pi$ -electron bond orders on excitation.

The effect of the conformational changes on the vibrational structure of the electronic transitions is discussed in section II.

(13) C. Eckart, *Phys. Rev.*, **47**, 552 (1935).



**Figure 3.** The ground and excited adiabatic potentials for torsion about the 6-7 bond of  $\beta$ -ionone. The dotted line is the ground state "free energy" surface at room temperature (see text).



**Figure 4.** The ground and excited adiabatic potentials for torsion about the 12-13 bond of 11-*cis*-retinal, relative to the all-*trans* energy as zero. The dotted line is the ground state "free energy" surface at room temperature (see text).

**Torsional Potentials.** Previous studies of ground and excited state potential surfaces of retinal<sup>3,14-18</sup> have restricted themselves to the subspace of torsional angles. Thus, the mapping of the energy along specific torsional angles did not account for the possible relaxation of steric repulsion by bond stretching and bond angle bending. As was shown in calculations for the ground state,<sup>6</sup> the heights of the torsional barriers decrease significantly if the bond angles are allowed to vary. To incorporate the effect of steric relaxation in the complete conformational space into the calculation,

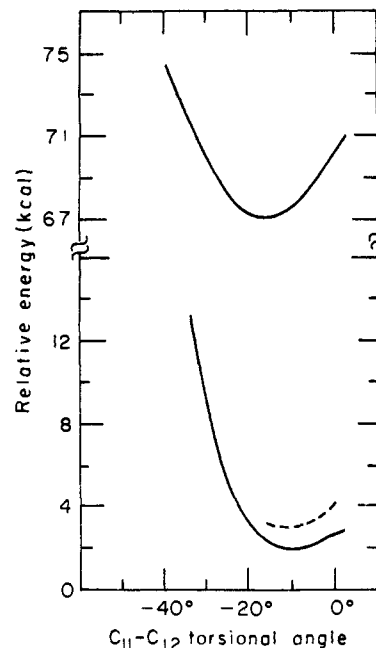
(14) H. A. Nash, *J. Theor. Biol.*, **22**, 314 (1969).

(15) B. Pullman, J. Langlet, and H. Berthold, *J. Theor. Biol.*, **23**, 482 (1969); J. Langlet, B. Pullman, and H. Berthold, *J. Mol. Struct.*, **6**, 139 (1970); J. Langlet and C. Giessner-Prettre, *ibid.*, **13**, 317 (1972).

(16) B. Honig and M. Karplus, *Nature (London)*, **229**, 558 (1971).

(17) B. Honig, B. Hudson, B. D. Sykes, and M. Karplus, *Proc. Nat. Acad. Sci. U. S. A.*, **68**, 1289 (1971).

(18) R. S. Becker, K. Inuzuka, and D. E. Balke, *J. Amer. Chem. Soc.*, **93**, 38 (1971).



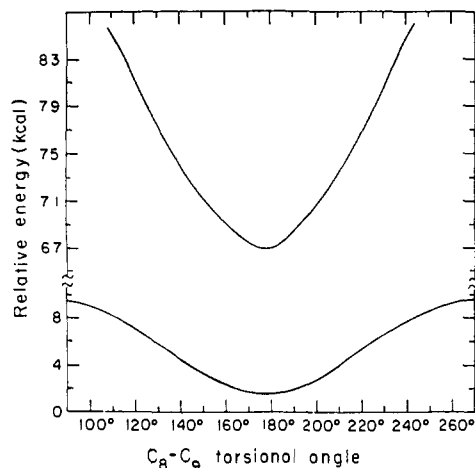
**Figure 5.** The ground and excited adiabatic potentials for torsion about the 11-12 bond of 12-*s-cis*-retinal, relative to the all-*trans* energy as zero. The dotted line is the ground state "free energy" surface at room temperature (see text).

we obtain effective one-dimensional torsional potentials by an "adiabatic" mapping procedure. In this procedure the energy is minimized with respect to all coordinates except a specific torsional angle which is chosen as the "adiabatic" variable.

The ground and excited state adiabatic potentials for torsion around certain bonds of interest are shown in Figures 3, 4, and 5. In each case, only the part of the potential in the neighborhood of the ground state minimum is shown; for more complete ground state results, see ref 6. Figure 3 represents rotation around the 6-7 bond in  $\beta$ -ionone; Figure 4 rotation about the 12-13 bond in 11-*cis*-retinal, and Figure 5 rotation about the 11-12 bond in 11-*cis*-retinal. The results for the 6-7 bond for all the retinals are similar to those shown in Figure 3, although there is significant variation in the value calculated for the torsional angle at the ground state minimum ( $-40^\circ$  in  $\beta$ -ionone,  $-50^\circ$  in all-*trans*-retinal,  $-40^\circ$  in 11-*cis*, 12-*s-cis*-retinal).

For the bonds 6-7 and 12-13 which are formally single bonds in the ground state, we see comparable behavior on excitation. The essential point in both cases is the increased  $\pi$ -bond order in the excited state in the presence of the steric repulsion, which prevents formation of a completely planar system. Defining the  $\pi$ -bond order as the coefficient of  $2^{\lambda}\beta_{\nu\mu}$  in the energy  $V^N(\mathbf{r})$  with  $\mathbf{r} = \mathbf{r}_0$  for the given state (eq 1 and 2; see also eq 17 and 26 of ref 4), we have for the 6-7 bond a value of 0.391 in the excited state vs. 0.260 in the ground state; for the 12-13 bond, the respective values are 0.634 vs. 0.355. It should be noted that the correct excited state bond order is somewhat different from the corresponding approximate bond order obtained by considering only a single excited molecular orbital without CI treatment; e.g., for the 6-7 bond, the correct excited state bond order is 0.391 while the approximate value is 0.41.

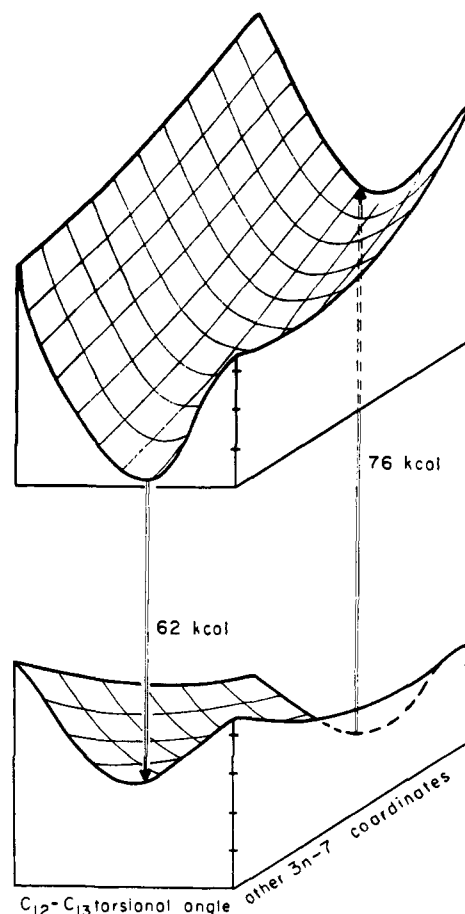
Figure 6 shows for comparison the potential ob-



**Figure 6.** The ground state and excited state adiabatic potential for torsion about the "normal" 8-9 bond of 11-*cis*,12-*s-cis*-retinal, relative to the all-trans energy as zero.

tained for the 8-9 bond in the two states. Here we have a corresponding increase in bond order (0.548 *vs.* 0.348) but no steric repulsions. For both states, the 8-9 bond potential has its minimum in the planar geometry and is well approximated by a parabola in the neighborhood of the minimum with the excited state having a considerably larger force constant than the ground state. Comparing Figures 3 and 4 with Figure 6, we see that the excited state potential for the bonds 6-7 and 12-13 has a general form which can be characterized as being narrower and steeper than the ground state potential. However, there are a number of additional points that are important. First, as expected because of the higher bond order, the excited state minimum for both 6-7 and 12-13 is closer to the planar configuration than the ground state minimum (see also Tables I-III). Second, in contrast to what is usually assumed,<sup>9,10</sup> the excited state curvature near the minimum is not very different from that in the ground state. Thus, the force constants obtained for the two states in a harmonic treatment would be rather similar. Where the two potentials differ significantly is for large displacements from the minimum. As can be seen from the figures, the ground state is more anharmonic than the excited state. A qualitative effect on the spectrum of these features of the potential could be to produce a significant temperature dependence; that is, with increasing temperature the spectrum could shift to shorter wavelengths and additional broadening could appear. Details concerning the spectra calculated for the molecules under consideration are given in the next sections.

An aspect of the calculation, which is not included in the simplified treatments of one-dimensional torsional surfaces,<sup>14-17</sup> is illustrated in Figure 7. In this figure the energy surface is drawn in two dimensions: one is the adiabatic torsional coordinate of the 12-13 bond and the other is an effective coordinate which represents all the other  $3n - 7$  internal coordinates. On the front face of the boxes that frame the excited and ground state surfaces are drawn curves appropriate for vertical emission from the excited state; that is, the molecular geometries used for obtaining *both* curves are those determined by adiabatic variation of the 12-13 bond in the *excited* state. Correspondingly, on the rear face of the box are drawn curves appropriate for vertical ab-



**Figure 7.** The ground state and excited state potential surfaces of 11-*cis*,12-*s-cis*-retinal. The surfaces are drawn schematically in two dimensions: one is the adiabatic  $\phi_{12-13}$  coordinate and the other is a representation of the other  $3n - 7$  coordinates (see text).

sorption from the ground state, in that the molecular geometries from an adiabatic calculation for twisting around the 12-13 bond in the *ground* state were used (*i.e.*, these curves are the same as the ones in Figure 4). The connection of the two curves in Figure 7 to form surfaces for the ground and excited states is arbitrary but helps to clarify the changes that occur as a function of geometry. It is clear from the figure that a simple one-dimensional model for torsion in which the same ground and excited curves are used for absorption and emission would yield an inaccurate picture of the spectrum. Of most importance in producing the difference between the two sets of curves are the bond length alterations on excitation, though other coordinates contribute as well.

In the double bond potential shown in Figure 5 for bond 11-12, the situation is essentially the reverse of that for the single bonds. It is seen that, as expected from the decrease in bond order on excitation (0.590 *vs.* 0.875), the minimum shifts away from planarity and the curve rises more slowly for negative angles. In going toward the planar geometry, the excited state potential rises more steeply than does that for the ground state.

## II. Vibronic Transition Intensities

Since the details of the methods for evaluation of vibronic transition intensities are being presented separately,<sup>5,19</sup> we outline here only the main points. For

(19) A. Warshel and M. Karplus, to be submitted for publication.

the calculated minimum energy geometries of the ground and excited state, the second derivatives of the potential are determined and used for a complete evaluation of the normal modes. It is then assumed that the relative vibronic intensities can be approximated by the square of the vibrational overlap integral (in the harmonic approximation)

$$I(\mathbf{m}, \mathbf{n}) = [C(\mathbf{m}, \mathbf{n})]^2 = \left[ \int \psi_{\mathbf{m}}^M(\mathbf{Q}^M) \psi_{\mathbf{n}}^N(\mathbf{Q}^N) d\mathbf{Q}^M \right]^2 \quad (3)$$

where  $\mathbf{m}$  and  $\mathbf{n}$  are the vectors of vibrational quantum numbers and  $\mathbf{Q}^M$  and  $\mathbf{Q}^N$  are the nuclear displacement coordinates of the two electronic surfaces,  $M$  and  $N$ , respectively. The equilibrium coordinates (in the Cartesian representation) and the normal mode vectors for the two states are referred to a single coordinate system by an Eckart transformation.<sup>13</sup> The resulting relationship between the two sets of coordinates is

$$\mathbf{Q}^N = \hat{\mathcal{L}}^N \mathcal{L}^M \mathbf{Q}^M - \hat{\mathcal{L}}^N \mathbf{\Delta} \quad (4)$$

where  $\mathbf{\Delta} = \mathbf{M}^{1/2}(\mathbf{r}_e^M - \mathbf{r}_e^N)$  is the mass scaled shift in equilibrium coordinates and the  $\mathcal{L}$ 's are the matrices of Cartesian normal coordinate vectors;  $\hat{\mathcal{L}}$  is the transpose of  $\mathcal{L}$ . Given eq 4, the overlap integrals,  $C(\mathbf{m}, \mathbf{n})$ , are evaluated using the generating function for the many-dimensional harmonic oscillator. For the transitions from the ground vibrational state of  $N$  to the state of  $M$  in which only the  $s$  vibrational mode is excited to the  $j$ th level, we have

$$C(\mathbf{m}_s^j, \mathbf{0}) = C(\mathbf{0}, \mathbf{0}) (-1)^j (j!)^{-j/2} [K_s^M / 2]^{j/2} H_j[\{a_s^M / (2K_s^M)\}^{1/2}] \quad (5)$$

where  $\mathbf{m}_s^j$  represents the appropriate  $\mathbf{m}$  vector. The quantities  $a_s^M$  and  $K_s^M$  are, respectively, the effective change in equilibrium coordinates and vibrational frequency for the  $s$  mode of the  $M$  state;  $H_j$  is the Hermite polynomial of the  $j$ th order. In the general treatment both  $a_s^M$  and  $K_s^M$  include contribution from all of the active normal modes of the state  $N$ . Starting with eq 5 for  $C(\mathbf{m}_s^j, \mathbf{0})$  and the corresponding expression for  $C(\mathbf{0}, \mathbf{n}_i^i)$ , it is possible to evaluate the intensities of transitions to combination levels by recursion formulae.<sup>19</sup> However, we make use in the present calculations of the approximate relation

$$C(\mathbf{m}, \mathbf{0}) = \prod_s C(\mathbf{m}_s^j, \mathbf{0}) \quad (6)$$

which we have shown to yield accurate results in model calculations.<sup>5, 19</sup> In addition, the effect of frequency changes ( $K_s^M$ ) was neglected for retinal, as we found in the calculation for  $\beta$ -ionone that they were of secondary importance. Thus, the main element, other than more complete treatment of the potential surfaces, included in the present calculations and not in most other treatments of polyatomic molecules is the nondiagonal nature of the transformation matrix  $\hat{\mathcal{L}}^N \mathcal{L}^M$ ; this is sometimes referred to as the "Dushinsky effect."<sup>20</sup>

The results of the calculations for  $\beta$ -ionone, *all-trans*-retinal, and 11-*cis*,12-*s-cis*-retinal (all in the harmonic approximation) are given in Tables V, VI, and VII, respectively; only the frequencies which have significant intensity ( $I_i^s/I_0 \geq 0.01$ ) are included in the

(20) F. Dushinsky, *Acta Physicochim. USSR*, 1, 551 (1937); G. J. Small, *J. Chem. Phys.*, 54, 3300 (1971).

Table V. Calculated Vibronic Transition Intensities of the  $\pi\pi^*$  Transition of  $\beta$ -Ionone<sup>a</sup>

Description <sup>b</sup>	$\nu_s$	$I_1^s/I_0$	$I_2^s/I_0$	$I_3^s/I_0$
C=C st + C=O st	1617	0.76	0.29	0.07
C=O st + C=C st	1558	0.23	0.02	
C=C st	1552	0.25	0.03	
C-C st + C-C-H ben	1315	0.26	0.04	
C-C st + C-C-H ben	1306	0.15	0.01	
C-C st + C-C-H ben	1268	0.05		
C <sub>5</sub> -CH <sub>3</sub> st	1086	0.05		
C-H oop + C <sub>1</sub> -CH <sub>3</sub> st	914	0.04		
C-H oop + C-C (ring) st	866	0.05		
C-H oop	740	0.11		
C-C-C (ring) ben	677	0.04		
C-C-C ben + tor	567	0.18	0.02	
C <sub>5</sub> -CH <sub>3</sub> oop	433	0.06		
C <sub>5</sub> -CH <sub>3</sub> oop + tor	391	0.16		
Tor + C-CH <sub>3</sub> oop	342	0.03		
Tor + C-CH <sub>3</sub> oop	330	0.10		
C <sub>6</sub> -C <sub>7</sub> tor	285	0.72	0.25	0.06
C <sub>1</sub> -CH <sub>3</sub> tor	246	0.06		
C <sub>5</sub> -CH <sub>3</sub> tor	233	0.07		
Tor	139	0.12		
Tor (ring)	102	0.70	0.18	0.02
Skeletal wag + tor	88	5.7	16.0	29.2
	66	0.06		
	49	0.13		

<sup>a</sup>  $I_i^s$  is the intensity of the  $0 \rightarrow i$  transition of the  $s$ th mode. <sup>b</sup> St = stretching; ben = bending; oop = out of plane; tor = torsion; wag = wagging.

Table VI. Calculated Vibronic Intensities of the  $\pi\pi^*$  Transition of *all-trans*-Retinal<sup>a</sup>

$\nu_s$	$I_1^s/I_0$	$I_2^s/I_0$	$I_3^s/I_0$
1639	0.19	0.03	
1627	0.86	0.40	0.14
1378	0.01		
1340	0.03		
1261	0.28	0.05	
1227	0.03		
1038	0.07		
965	0.05		
912	0.05		
881	0.03		
714	0.02		
575	0.03		
508	0.02		
397	0.03		
345	0.04		
343	0.05		
260	0.03		
246	0.05		
202	0.03		
173	0.09		
160	0.02		
111	0.23	0.03	
97	0.14	0.02	
67	0.03		
56	2.00	2.08	1.50
41	0.69	0.27	0.08
35	1.28	0.88	0.42
20	0.25	0.04	

<sup>a</sup> Notation as in Table V.

tables. For each contributing vibrational mode of  $\beta$ -ionone and 11-*cis*,12-*s-cis*-retinal, an indication is given of its major internal coordinate components; some of the most important normal modes are illustrated in Figures 8 and 9. For *all-trans*-retinal, most of the contributing modes can be identified by their correspondence with 11-*cis*,12-*s-cis* so that we have not given a complete description in the table. How-

**Table VII.** Calculated Vibronic Transition Intensities of the  $\pi\pi^*$  Transition of 11-*cis*,12-*s-cis*-Retinal<sup>a</sup>

Description	$\nu_s$	$\nu_{s'}$	$I_1^s/I_0$	$I_2^s/I_0$	$I_3^s/I_0$
C—H (CH <sub>3</sub> ) st	2899	2899	0.02		
C=C st	1652	1680	0.02		
	1620	1660	0.71	0.28	0.08
	1606	1646	0.13	0.02	
	1572		0.08		
	1521	1565	0.15	0.02	
C—C st + C—C—H ben	1400	1415	0.02		
	1356	1368	0.04		
	1329		0.03		
	1321	1308	0.11	0.01	
	1321	1302	0.05		
	1304	1270	0.06		
	1249	1198	0.05		
	1157		0.03		
	1140		0.02		
C—CH <sub>3</sub> st	1044	1063	0.06		
C—CH <sub>3</sub> st	981	1000	0.06		
C—C—C ben + C—CH <sub>3</sub> st	991	936	0.09		
C—H oop + C—C—C ben	806		0.01		
C—C—C ben + C—CH <sub>3</sub> oop	653	664	0.01		
C—C—C ben + oop	574		0.04		
C—C—C ben	543	556	0.11	0.01	
C—C—C ben (ring) + tor	495		0.01		
C—C—C ben + tor	438	443	0.07		
	424	424	0.06		
	407	406	0.13	0.01	
Tor + C—CH <sub>3</sub> oop	399		0.08		
	376	343	0.03		
	353	326	0.04		
	334	286	0.28	0.05	
Tor	293	270	0.38	0.09	
	265		0.03		
	262	247	0.09		
	216	202	0.13	0.01	
	198	189	0.06		
Skeletal wag + tor	169		0.01		
	137		0.01		
	126	127	0.02		
	100	103	0.04		
	85	83	0.52	0.16	0.03
	80		0.03	0.06	
	56	55	1.35	0.97	0.49
	39	40	0.29	0.05	
	26	29	5.1	13.6	24.3
	17	17	1.1	0.65	0.27

<sup>a</sup> Notation as in Table V;  $\nu_s$  are ground state frequencies corresponding to the excited states modes in the same row and having strong Franck-Condon factors for fluorescence from the  $\pi\pi^*$  state.

ever, it should be noted that there are fewer contributions with significant intensity ( $I_1^s/I_0 \geq 0.01$ ) in *all-trans*-retinal than in the 11-*cis* compound.

Many vibronic transitions (not included in the table) are essentially forbidden. This can be a consequence of the fact that there is no associated origin shift (e.g., CH stretching vibrations) or that there is an effective symmetry selection rule (e.g., asymmetric C=C stretching vibrations). In either case, the projection of the conformational change on the corresponding normal-mode vectors is small. It is clear from Tables V and VII that the dominant  $0 \rightarrow 1$  vibronic excitations involve C=C (as well C=O) and C—C stretching and torsion of the 6–7 or 12–13 (in 11-*cis*,12-*s-cis*) bonds combined with skeletal wagging motion. A variety of other normal coordinates involving C—C—C bending, C—C—H bending, and C—CH<sub>3</sub> motion also contribute significantly.

Although the absorption spectra of  $\beta$ -ionone and the retinals are diffuse, some comparisons can be made with recent resonance Raman studies of *all-trans*- and 11-*cis*-

retinal in solution.<sup>21</sup> In such measurements, the dominant peaks correspond to the ground state vibrations strongly coupled to the resonant vibronic transitions, although a quantitative determination of relative intensities and their dependence on the incident wavelength requires a more detailed treatment. Without that, which is outside the scope of this paper, it is not worthwhile to consider specifically the matrix elements between the two vibrational states of the ground electronic state and the excited vibronic states involved in the Raman scattering. Instead we assume simply, as should be a reasonable approximation for the present case, that the ground state normal modes which play an important role in the Raman spectrum correspond to those Franck-Condon active in the electronic absorption spectrum. Table VII lists for 11-*cis*,12-*s-cis*-retinal the values of the ground state vibrational frequencies  $\nu_{s'}$  which appear to correspond to the Franck-Condon active modes  $\nu_s$ . There is generally good agreement between the experimental results and the calculations, although there are significant differences in the values of the frequencies. Thus, the strongest mode in the region studied experimentally is at 1577  $\text{cm}^{-1}$ , while that obtained in the calculations is at 1660  $\text{cm}^{-1}$ ; it is clearly a C=C stretching mode in both cases. The difference is mainly due to the fact that our potential surfaces overestimated the symmetric C=C stretching modes in polyenes by 60–80  $\text{cm}^{-1}$ ; e.g., in *trans*-hexatriene the calculated frequency is 1689  $\text{cm}^{-1}$  compared with the observed value of 1623  $\text{cm}^{-1}$ . It should be mentioned also that there are other C=C stretching modes (1645 and 1565  $\text{cm}^{-1}$ ) which are calculated to have significant vibronic intensities. The line which correspond to the calculated mode at 1645  $\text{cm}^{-1}$  may be hidden in the region of the 1577- $\text{cm}^{-1}$  peak; the line which corresponds to the 1565- $\text{cm}^{-1}$  mode is not apparent in the spectrum. There are a series of observed bands in the region 1400–1126  $\text{cm}^{-1}$ , which correspond to calculated contributions of C—C stretching and C—C—H bending modes. Finally, there are three observed peaks in 11-*cis*-retinal (1018, 999, and 965  $\text{cm}^{-1}$ ) which appear to correspond to the calculated values of 1063, 1000, and 936  $\text{cm}^{-1}$ ; all of these involve significant contributions from C—CH<sub>3</sub> stretching. In addition, the calculations show (see Table VII) a number of lower frequency modes, mainly involving torsion, that have large Franck-Condon factors. It would be very interesting to have resonance Raman measurements in the appropriate frequency region. In 11-*cis*-retinal, and not in *all-trans*, a C—H stretching mode (2899  $\text{cm}^{-1}$ ) of the 13 CH<sub>3</sub> group makes a nonnegligible contribution.

It is important to note that the strongest vibronic progressions (88  $\text{cm}^{-1}$  in  $\beta$ -ionone, 56  $\text{cm}^{-1}$  in *all-trans*-retinal, 56 and 26  $\text{cm}^{-1}$  in 11-*cis*,12-*s-cis*-retinal) are not pure torsional transitions, though they do all have significant torsional components. For example, the 88- $\text{cm}^{-1}$  mode of  $\beta$ -ionone is shown in Figure 8 to involve a considerable amount of skeletal wagging, as indicated by the large motion of the chain atoms. Similar results are seen in the other modes shown in Figures 8 and 9. These imply that a quantitative description of such sterically hindered molecules in terms

(21) D. Gill, M. E. Heyde, and L. Rimai, *J. Amer. Chem. Soc.*, **93**, 6289 (1971); M. E. Heyde, D. Gill, R. G. Kilponen, and L. Rimai, *ibid.*, **93**, 6776 (1971).

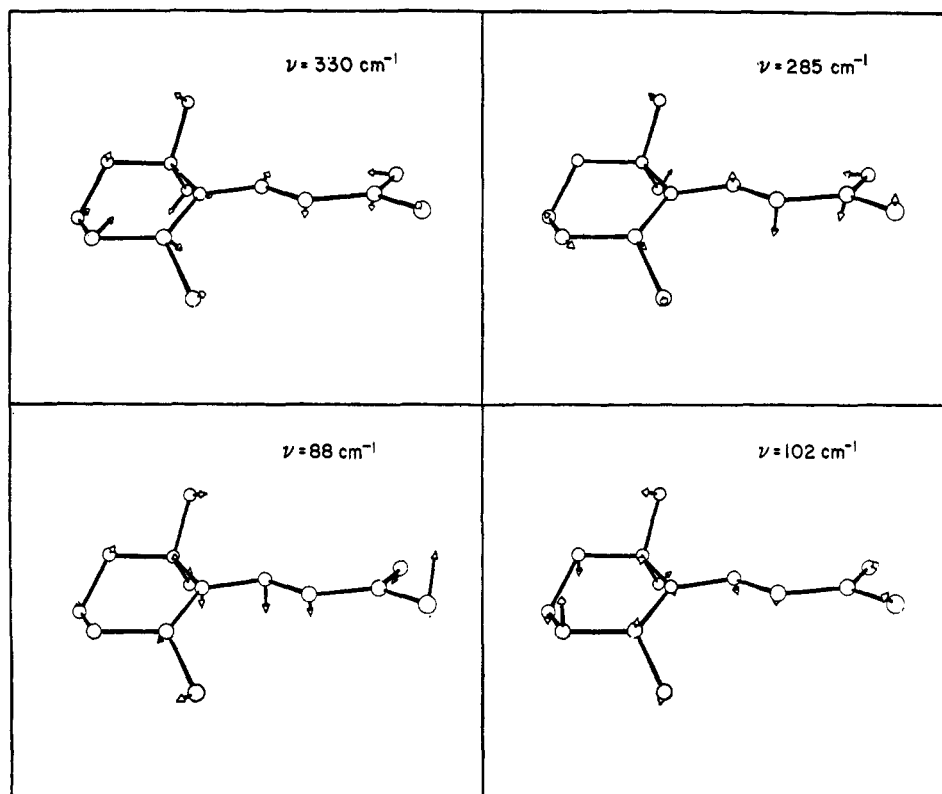


Figure 8. Selected modes of  $\beta$ -ionone with significant torsional components that contribute to the vibronic spectrum.

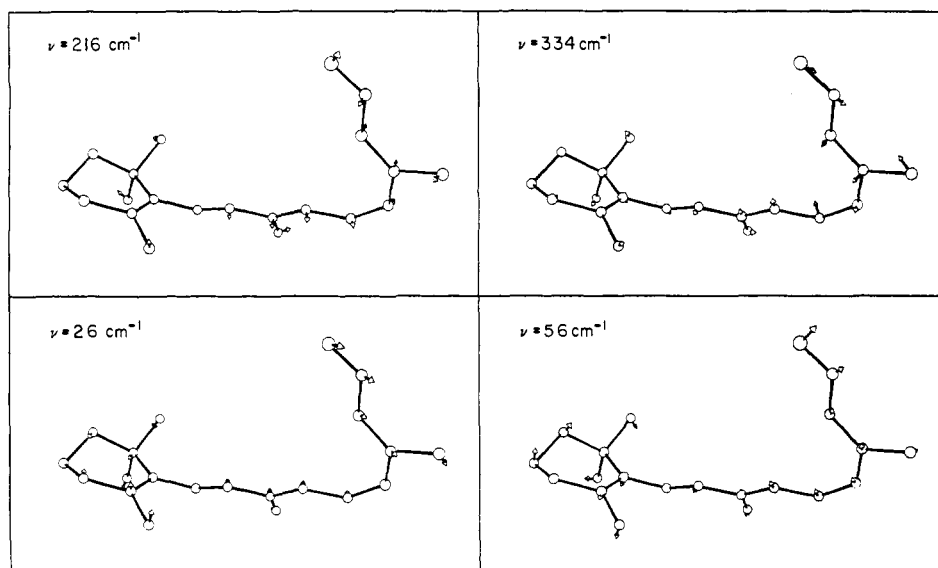


Figure 9. Selected modes of 11-*cis*,12-*s-cis*-retinal with significant torsional components that contribute to the vibronic spectrum.

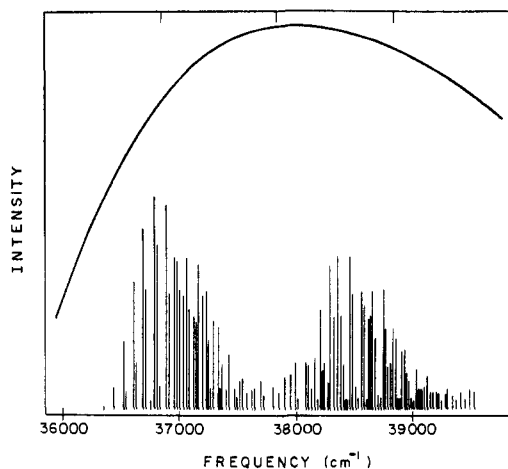
of torsion around individual bonds (6-7 in  $\beta$ -ionone, 6-7 and 12-13 in 11-*cis*-retinal) is not valid, though such a simplification may still be useful for qualitative discussions (see below).

In comparing the strongest progressions of  $\beta$ -ionone and the two retinal isomers (Tables V-VII), we see an interesting difference. The 88- $\text{cm}^{-1}$  progression of  $\beta$ -ionone, which is by far the strongest, corresponds most closely to the much weaker 56- $\text{cm}^{-1}$  vibration in the retinals. The difference in vibronic intensity appears to be due primarily to the smaller 6-7 angle change calculated for the retinals ( $\Delta \approx 7-8^\circ$ ), relative to that in

$\beta$ -ionone ( $\Delta \approx 20^\circ$ ). Comparison of *all-trans*- with 11-*cis*-retinal shows that the dominant progression in the latter (26  $\text{cm}^{-1}$ ) is essentially absent in the former. This is of course the vibration which can be approximately described as torsion about the 12-13 bond (see Figure 9), though other internal modes contribute as well.

From the calculated  $I_i^s$  values, as given in Tables V-VII for the lower vibronic transitions, and from eq 6 for the combination bands, the vibronic intensities of the  $\pi\pi^*$  transition can be obtained; it should be noted that all of the values are relative to the calculated vi-



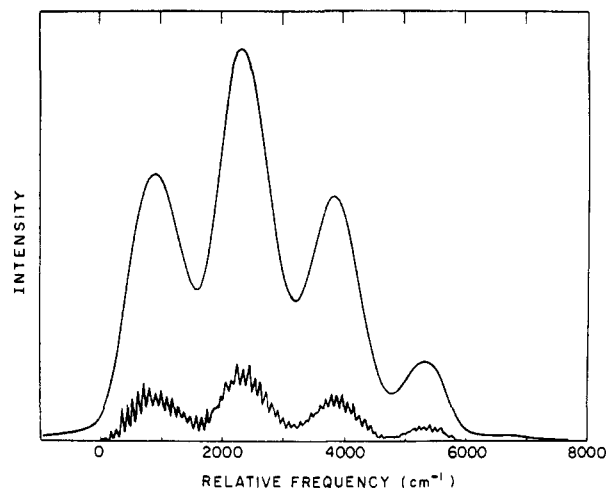


**Figure 10.** Calculated stick diagram of vibronic transitions in the  $\pi\pi^*$  transition of  $\beta$ -ionone; the 0,0 transition is at  $36,354\text{ cm}^{-1}$ . The experimental curve whose position and relative intensity are arbitrary is taken from ref 23.

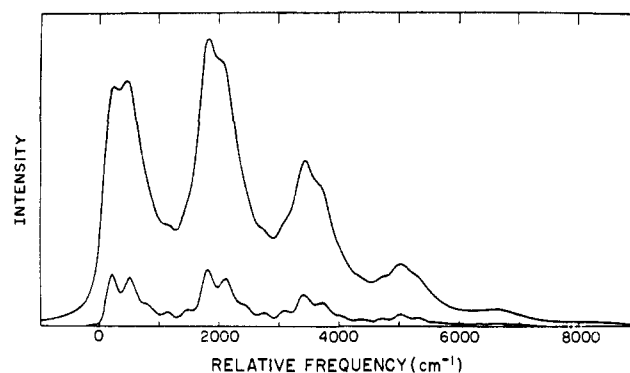
brational overlap of the  $0 \rightarrow 0$  transition. Figure 10 shows a stick diagram of the results obtained for  $\beta$ -ionone;<sup>22</sup> an experimental curve<sup>23</sup> that is arbitrarily positioned is included only to indicate the diffuseness of the observed spectrum. In the calculated results, the spacing of the two "bands" that are shown is due to the C=C bond stretching progression ( $1617\text{ cm}^{-1}$ ). Within each band, the dominant progression corresponds to the  $88\text{-cm}^{-1}$  mode. Its combination with other progression leads to a significant density of transitions but is not sufficient to completely "fill in" the  $1617\text{-cm}^{-1}$  progression. To examine this question further, we show in Figure 11, the results obtained for  $\beta$ -ionone with the assumption that each vibronic transition has a line width of  $1\text{ cm}^{-1}$  (lower curve) and  $200\text{ cm}^{-1}$  (upper curve). It is clear that the fine details of the spectrum are unresolved, particularly in the  $200\text{-cm}^{-1}$  widths drawing, but the  $1617\text{-cm}^{-1}$  progression remains. In Figure 11, it is the *second* band which is most intense although some of the individual lines in Figure 10 associated with the first band have the highest intensity; this type of effect was described already in ref 5.

Figure 12 shows the calculated spectrum for the strongly allowed  $\pi\pi^*$  transition of 11-*cis*,12-*s-cis*-retinal, again with  $1\text{ cm}^{-1}$  (lower curve) and  $200\text{ cm}^{-1}$  (upper curve) line widths. As in  $\beta$ -ionone, most of the structure in the individual bands is unresolved but the C=C progression remains. The double peak appearing in each of the bands with a spacing of  $\sim 300\text{ cm}^{-1}$  is a consequence of the presence of two strong vibrations of similar frequency ( $334$  and  $293\text{ cm}^{-1}$ ) which sum to give a strong combination band with the basic torsional transition.

It is clear that the calculations for isolated molecules of  $\beta$ -ionone and 11-*cis*,12-*s-cis*-retinal or for such molecules with normal solvent broadening ( $200\text{ cm}^{-1}$ ) do not yield the diffuse spectra observed for these species even at  $77^\circ\text{K}$ . One possibility which has been neglected in the present calculations is that the diffuse spectrum is produced by interaction between the car-



**Figure 11.** Calculated vibronic envelope of the  $\pi\pi^*$  transition of  $\beta$ -ionone; the assumed line width in the lower curve is  $1\text{ cm}^{-1}$  and in the upper curve is  $200\text{ cm}^{-1}$ .



**Figure 12.** The calculated vibronic envelope of the  $\pi\pi^*$  transition of 11-*cis*,12-*s-cis*-retinal; the assumed line width in the lower curve is  $1\text{ cm}^{-1}$  and in the upper curve is  $200\text{ cm}^{-1}$ . (The 0,0 transition is at  $23,259\text{ cm}^{-1}$ .)

bonyl  $n\pi^*$  state and the  $\pi\pi^*$  state. That near degeneracy of two such states can lead to some broadening has been demonstrated.<sup>24</sup> However, although the required near degeneracy is possible for the retinals, the  $\pi\pi^*$  state is certainly at a significantly higher energy than the  $n\pi^*$  state in  $\beta$ -ionone. Also, Christensen and Kohler<sup>25</sup> have shown recently that axerophytene, a hydrocarbon analog of retinal which lacks the  $n\pi^*$  transition, has a diffuse spectrum at  $77^\circ\text{K}$ . These results imply that, while the  $n\pi^*$  transition when present with the correct frequency can affect the  $\pi\pi^*$  transition, it cannot be the dominant factor in the series of molecules under consideration. Since it is also well known that unhindered polyenes<sup>9,10,26</sup> (e.g.,  $\text{CH}_3(\text{CH}=\text{CH})_n\text{CH}_3$ ) have well-resolved spectra under appropriate conditions, we are led to reexamine the possible role of sterically hindered torsional vibrations. As a model system we consider the 12-13 single bond in 11-*cis*,12-*s-cis*-retinal; it is of interest also for an analysis of the unusual temperature dependence of the spectrum in this compound (see section III). Calculations have been made in which the ground state potential was mod-

(24) R. Hochstrasser, *Accounts Chem. Res.*, **19**, 266 (1968).

(25) R. L. Christensen and B. E. Kohler, *Photochem. Photobiol.*, **18**, 293 (1973).

(26) L. Jurkowitz, J. N. Loeb, P. K. Brown, and G. Wald, *Nature (London)*, **184**, 614 (1959).

(22) The results shown in Figure 10 differ slightly from those in Figure 4 of ref 5 due to minor corrections in the calculations.

(23) R. L. Christensen, private communication.

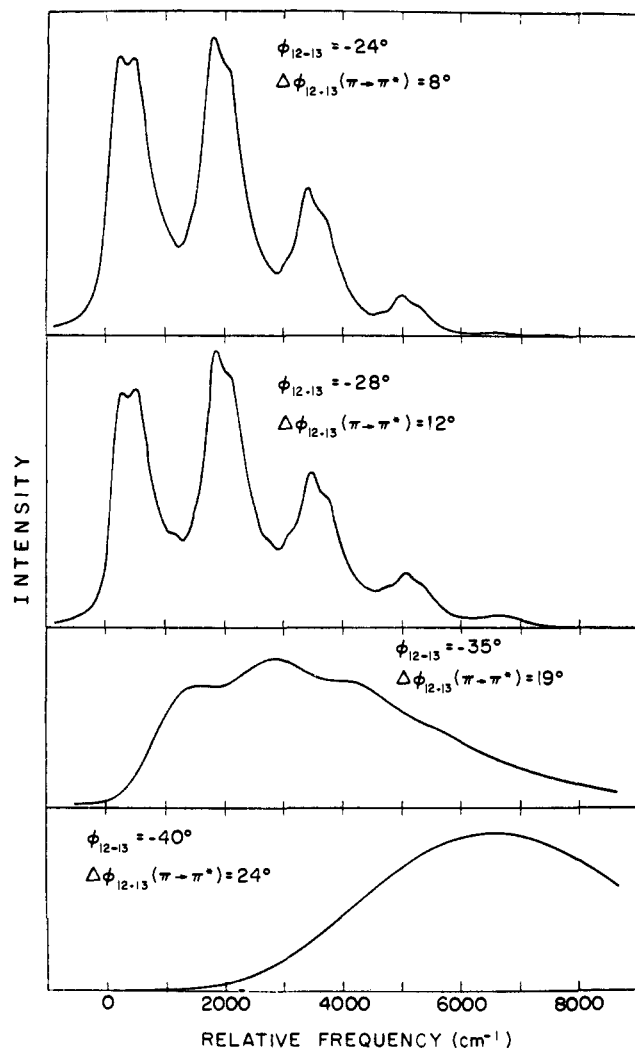


Figure 13. The vibronic structure of the  $\pi\pi^*$  transition of 11-*cis*,12-*s-cis*-retinal as a function of the  $\phi_{12-13}$  ground state torsional angle; a  $200\text{-cm}^{-1}$  line width was used (see text).

ified so that the equilibrium value of  $\phi_{12-13}$  was shifted to different points.<sup>27</sup> At each point we calculated the relative intensities of transitions to the vibronic levels of the excited state potential; the latter was kept unaltered because it is steeper than the ground state. The results obtained for a number of different  $\phi_{12-13}$  angles are shown in Figure 13. The second curve from the top ( $\phi_{12-13} = -28^\circ$ ) is that for the calculated minimum of

(27) The procedure by which the equilibrium value of  $\phi_{12-13}$  is modified so as to obtain the corresponding normal modes for the calculation is as follows. A fictitious potential  $V'(\phi_{12-13}) = K'\phi_{12-13}$  is added to the ground state potential  $V^0(r)$ . The parameter  $K'$  is adjusted so that the minimum of the potential  $V^0 + V'$  with respect to all Cartesian coordinates corresponds to the desired equilibrium value of  $\phi_{12-13}$ ; an analogous procedure is used for obtaining the adiabatic potential curves. The ground state normal modes required for calculation of the vibronic transition intensities are obtained by diagonalization of the mass scaled second derivative matrix of  $V^0 + V'$ . The calculation is done at a point in which the gradient of  $V^0 + V'$  is zero and the matrix of second derivatives with respect to Cartesian coordinates is invariant to rotation and translation. The resulting  $3n - 6$  normal coordinates are thus orthogonal to the rotation and translation normal modes. Once the  $3n - 6$  normal coordinates are computed,  $V'$  is omitted and the second derivatives of  $V^0$  with respect to these normal coordinates are evaluated and treated as the harmonic frequencies (at the particular value of  $\phi_{12-13}$ ). The first derivatives of  $V^0$  and the cross-term second derivatives can be treated as a perturbation. However, we can ignore them here because the ground state potential is shallow (so the first derivatives are small) and the second derivatives of  $V'$ , which is linear with  $\phi$ , are small; i.e., the cross terms which are due to the differences between the second derivatives of  $V^0$  and  $V^0 + V'$  are negligible.

the ground state potential and is identical with the corresponding curve in Figure 12; of the three other curves in Figure 13, the top one has a twist from planarity that is smaller than the calculated value, and the two lower curves have larger twists. Since for all of the curves the excited state surface is unchanged and has its minimum at  $-16^\circ$ , the change in  $\phi_{12-13}$  on excitation (indicated as  $\Delta\phi_{12-13}$  in the figure) increases as  $\phi_{12-13}$  for the ground state becomes more negative. It is clear from the figure and in accord with expectations that for larger  $\Delta\phi_{12-13}$  the spectrum broadens and shifts to higher frequencies. In particular, for values of  $\Delta\phi_{12-13}$  greater than  $\approx 20^\circ$ , an essentially diffuse spectrum results. To indicate the sources of the change in the spectrum, we present in Table VIII the calculated relative Franck-Condon

Table VIII. Calculated Vibronic Structure of the  $\pi\pi^*$  Transition from the Conformational Point  $\phi_{12-13} = -35^\circ$  of 11-*cis*,12-*s-cis*-Retinal<sup>a</sup>

$\nu_s$	$I_1^s/I_0$	$I_2^s/I_0$	$I_3^s/I_0$	$\nu_s$	$I_1^s/I_0$	$I_2^s/I_0$	$I_3^s/I_0$
3077	0.01			786	0.04		
2963	0.06			732	0.11	0.01	
2962	0.06			653	0.07		
2899	0.23	0.04		574	0.10		
1652	0.02			543	0.07		
1640	0.02			454	0.06		
1620	0.63	0.23	0.06	438	0.12	0.01	
1606	0.11	0.01		407	0.13	0.01	
1572	0.08			353	0.23	0.04	
1529	0.06			334	1.22	0.80	0.37
1521	0.31	0.06		293	0.80	0.35	0.11
1506	0.02			275	0.03		
1409	0.02			265	0.03		
1356	0.04			262	0.16	0.02	
1312	0.10			216	1.13	0.69	0.30
1304	0.08			198	0.33	0.07	
1249	0.13	0.02		169	0.09		
1168	0.02			137	0.10	0.01	
1157	0.05			100	0.86	0.41	0.1
1140	0.13			85	2.35	2.86	2.41
1062	0.04			80	0.30	0.06	
1044	0.06			56	2.71	3.8	2.7
1000	0.07			39	0.63	0.23	0.06
956	0.06			26	9.65	46.9	153.9
911	0.37	0.08		17	3.20	5.2	5.9
806	0.14	0.02					

<sup>a</sup> Notation as in Table V.

factors for  $\phi_{12-13} = -35^\circ$ . Comparing this table with Table VII, we see that a large number of vibrations with an important torsional component are significantly increased in intensity (e.g., 334, 216, 85, 56, 26, 17  $\text{cm}^{-1}$ ); it is the contributions from these modes and their combination bands that fill in the spectrum. Also, some of the C=C (e.g., 1521  $\text{cm}^{-1}$ ) and the methyl C-H stretching (e.g., 2899  $\text{cm}^{-1}$ ) progressions become more active as a result of their coupling with the torsional modes. The apparent shift in the spectrum which begins to be evident at  $\phi_{12-13} = -35^\circ$  and becomes very large at  $\phi_{12-13} = -40^\circ$  is mainly a consequence of the rapid rise in intensity of the torsional modes with excitation; that is, in analogy to ethylene, for a large change in the torsional angle between the two electronic states, only the highly excited torsional modes contribute significant intensity and the transition becomes effectively Franck-Condon forbidden.

Model calculations for the sterically hindered 6-7 bond in  $\beta$ -ionone, which we do not present here, show

exactly corresponding results; *i.e.*, sufficiently large changes in the ground state equilibrium torsional angle ( $\sim 12^\circ$ ) lead to a completely diffuse spectrum. It is, of course, the 6–7 bond which would have to be involved in  $\beta$ -ionone and *all-trans*-retinal, since there is no other sterically hindered linkage in these molecules. In 11-*cis*-retinal, both the 6–7 and the 12–13 bonds could contribute to the diffuse spectrum.

By utilizing the model calculations, it is possible to suggest several interpretations of the experimental results but not yet to provide a unique analysis. An important question in this regard is whether the completely diffuse spectra are intrinsic properties of individual molecules; *i.e.*, would a molecule with a unique geometry in a unique site of a mixed crystal have a diffuse spectrum at low temperature? If so, it would appear necessary that the calculated potential functions be sufficiently in error to yield the geometry change required for a diffuse spectrum. This is not impossible, as from Figure 3 the ground state torsional potential is very flat and small alterations of the parameters could result in a significant change of the equilibrium angle. One point against this suggestion is that the calculated torsional angles for the ground state of *all-trans*- and 11-*cis*,12-*s-cis*-retinal are in rather good agreement with the X-ray values,<sup>6,28</sup> which, however, could be partly a consequence of crystal perturbations. A related factor, not included in the calculations, is the strong anharmonicity of the torsional potentials. Model calculations for  $\beta$ -ionone using the third and fourth derivatives with respect to Cartesian coordinates<sup>29</sup> at the calculated minima indicate that this type of anharmonic effect is not sufficient to account for the diffuse spectrum. This is a consequence of the fact that, although the anharmonicities of both the ground and excited state are significant, they are similar in magnitude and so have only a small effect on the spectrum. There is also a temperature-dependent change in the effective molecular conformation due to anharmonicity. This can be estimated by minimizing the geometry as a function of a potential which is the sum of the potential energy  $V^N(\mathbf{r})$  of eq 1 and the "vibrational free energy" at a given temperature. Practically, one evaluates the free energy along the adiabatic path of a given torsional angle.<sup>5,6</sup> The potentials for the various bonds including the corrections for the vibrational free energy at 300°K are shown as dashed lines in Figures 3, 4, and 5. There is a slight shift of the equilibrium torsional angles toward a somewhat larger negative value; *e.g.*, the difference in the 6–7 torsional angle of  $\beta$ -ionone between the vibrationless minimum and the 0°K minimum is  $2.5^\circ$  while the difference between 0 and 300°K is an additional  $2^\circ$ . This shift is due to steric interactions which produce an increase in the harmonic frequencies of certain bending vibrations upon a decrease in the magnitude of the torsional angle. However, as stated above, model calculations have shown that a shift of  $\sim 12^\circ$  in the ground state equilibrium angle (without changing the excited state surface) is needed to obtain complete diffuseness, while the free energy effect in our calculation is less than  $5^\circ$  at room temperature.

(28) R. G. Gilardi, I. L. Karle, J. Karle, and W. Sperling, *Nature (London)*, **232**, 187 (1971); T. Hamanaka, T. Mitsui, T. Ashida, and M. Kakudo, *Acta Crystallogr., Sect. B*, **28**, 214 (1972); R. D. Gilardi, I. L. Karle, and J. Karle, *ibid.*, **28**, 2605 (1972).

(29) A. Warshel, *J. Chem. Phys.*, **55**, 3372 (1971).

An additional factor which may play the dominant role in the observed diffuse spectrum is that due to the very broad nature of the ground state torsional potential, particularly around the 6–7 bond, molecules in slightly varying local environments may have their effective ground state minima over a range of torsional angles. Then, since the excited state potential surface (which is much steeper than the ground state surface) is less affected by the environment, the shift  $\Delta\phi$  of the equilibrium torsional angle upon excitation will vary from molecule to molecule. As a result, the vibronic structure will change significantly; *e.g.*, if as a consequence of solvent interaction a molecule has its minimum at the point  $\phi_{6-7} = -60^\circ$  (Figure 3), the torsional progressions will be extended to much higher energy than in the unperturbed molecule ( $\phi_{6-7} = -40^\circ$ ). The mixing of different vibronic distributions in which the maxima of some are strongly shifted (*e.g.*, mixing of the results of Figure 13) could lead to the structureless character of the spectrum. Model calculations for  $\beta$ -ionone have shown that it is possible to obtain complete diffuseness if the ground state equilibrium value of the 6–7 torsional angle is in the range of  $40$ – $50^\circ$  with an equal probability for each point in this region and the excited surface is kept unchanged.

The main reasons we have examined for the diffuseness of the spectrum depend in one way or another on the shallowness of the ground state torsional potentials relative to those in the excited state. This suggests a procedure for studying the origin of the diffuseness, as well as the effect of temperature on the spectrum. It is an extension of the method by which the results of Figure 13 were obtained. The quantum mechanical Franck–Condon factors are calculated for transitions from a set of accessible ground state points. The superposition of the resulting vibronic envelopes, weighted according to the relative population of the ground state points, is used to construct the electronic line shape. Such a procedure, called "quasi-classical vibronic mapping," can be used with Boltzmann weighting factors to study temperature-dependent changes in the spectrum (see section III).

### III. Temperature Dependence of the Spectrum

One of the important questions concerning the spectra of the retinal isomers is the large temperature dependence of the  $\pi\pi^*$  absorption of the 11-*cis* compound. As was shown by Jurkowitz, Loeb, Brown, and Wald in 1959,<sup>26</sup> there is a significant increase in the  $\epsilon_{\max}$  value of the transition in cooling from 300 to 80°K; *i.e.*, the ratio of  $\epsilon_{\max}$  for the temperature 300 and 80°K is  $\sim 1.6$  for 11-*cis*-retinal in EPA, while the corresponding ratio for *all-trans*-retinal is  $\sim 1.1$ . Also, both 11-*cis* and *all-trans* show a shift to the red in the position of the absorption maximum, which can be approximately accounted for by correcting for solvent contraction effects.<sup>30</sup> More detailed measurements which confirm the work of Jurkowitz, *et al.*, and include some of the higher transitions, have been made by Becker, Inuzuka, and Balke<sup>18</sup> and by Sperling and Rafferty.<sup>8</sup>

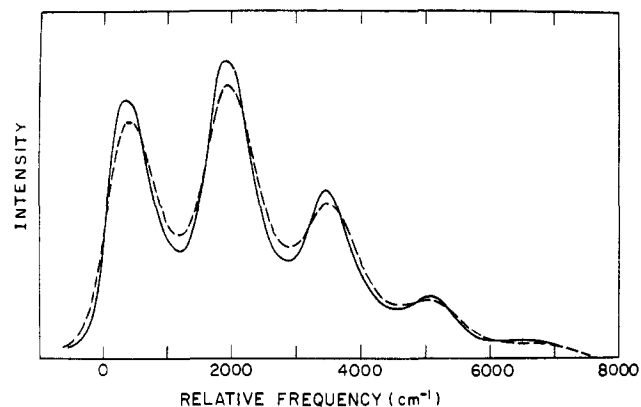
The observed changes in  $\epsilon_{\max}$  can be a consequence of two possible types of effects. One of these is the difference in the Franck–Condon overlap integrals for the various vibrational levels of the ground state, and the

(30) R. R. Birge, K. Schullen, and M. Karplus, to be published.

**Table IX.** Calculated Excitation Energies ( $E_i$ ,  $\text{cm}^{-1}$ ) and Oscillator Strengths (in Parentheses) for 11-*cis*-Retinal Conformers<sup>a</sup>

Conformation	$E_1$	$E_2$	$E_3$	$E_4$	$E_5$
11- <i>cis</i> , 12- <i>s-cis</i>	26797 (0.81)	36559 (0.77)	38025 (0.28)	44345 (0.20)	45000 (0.20)
11- <i>cis</i> , 12- <i>s-trans</i>	28550 (1.65)	37434 (0.27)	40208 (0.132)	44137 (0.11)	45450 (0.04)
11- <i>cis</i> , 12- <i>s-cis</i> , 8- <i>s-cis</i>	25842 (0.58)	30130 (0.57)	37522 (0.65)	44251 (0.11)	44829 (0.11)

<sup>a</sup> All torsional angles not listed are *trans*, except for the 6-7 angle which is distorted *s-cis*; the conformations used correspond to the calculated local minimum for each of the species considered.



**Figure 14.** The calculated vibronic envelope within the harmonic approximation of the  $\pi\pi^*$  transition of 11-*cis*,12-*s-cis*-retinal: (—) at 77°K (line width of 200  $\text{cm}^{-1}$ ), (---) at 300°K (line width of 200  $\text{cm}^{-1}$ ).

other is the dependence of the electronic transition moment integral on geometry. Considering the electronic transition moment first, we find that in the neighborhood of the minimum energy structure for 11-*cis*,12-*s-cis*-retinal, the effect of geometry changes is far too small; *i.e.*, since the oscillator strength increases by only 3% in going from a structure with  $\phi_{12-18} = -30$  to  $-40^\circ$ , thermal effects on the geometry due to the above mechanism cannot account for the observed temperature dependence.

There is the possibility that other 11-*cis* geometries with significantly different oscillator strengths might be involved. Two such 11-*cis* geometries, which have calculated energies close to the 11-*cis*, 12-*s-cis* isomer, are 11-*cis*, 12-*s-trans* and 11-*cis*, 12-*s-cis*, 8-*s-cis*.<sup>6</sup> In Table IX, we list the calculated transition frequencies and oscillator strengths for the three species; only the lower level results are significant, since some of the higher transitions may be strongly altered by the inclusion of double excitations.<sup>12</sup> It is seen that, as compared with 11-*cis*, 12-*s-cis*-retinal, the rotamer 11-*cis*, 12-*s-trans* has a much higher oscillator strength for the first  $\pi\pi^*$  transition, and 11-*cis*, 12-*s-cis*, 8-*s-cis* has a somewhat lower oscillator strength. Thus, an equilibrium between the two forms 11-*cis*, 12-*s-cis* and 11-*cis*, 12-*s-trans* or between 11-*cis*, 12-*s-cis*, 8-*s-cis* and 11-*cis*, 12-*s-cis* with the latter more stable in each case could lead to a temperature dependence of the type that is observed for the extinction coefficient.<sup>31</sup> Also, in correspondence with the Thomas-Kuhn sum rule, as the observed lowest  $\pi\pi^*$  transition in this model decreases in intensity, the higher  $\pi\pi^*$  transition should increase (see Table IX). In the spectra of Becker, *et al.*,<sup>18</sup> and particularly those of Sperling and Rafferty,<sup>8</sup>

(31) The pair 11-*cis*, 12-*s-cis* and 11-*cis*, 12-*s-trans* has been considered independently by A. Moscowitz, private communication, and by W. Sperling, private communication.

such a trend is apparently observed. In nmr studies of the ground state of 11-*cis*-retinal,<sup>6</sup> there is no indication of the presence of another species like 11-*cis*, 12-*s-cis*, 8-*s-cis*. The measurements do suggest, however, that in acetone the pair 11-*cis*, 12-*s-cis* and 11-*cis*, 12-*s-trans* are in equilibrium with the 11-*cis*, 12-*s-trans* conformer slightly more stable. Against this interpretation of the temperature dependence is that the effective shift and change in shape of the absorption peak looks more like a vibronic effect than the superposition of electronic transitions associated with two different isomers (see below). Also, for the pairs of molecules considered above, the species with the lower intensity transition is calculated to have its maximum at a longer wavelength than the higher intensity species, in disagreement with experiment. Calculations<sup>30</sup> including doubly-excited configurations lead to a second state in the same region of the spectrum; its presence reduces the expected shift in  $\lambda_{\text{max}}$  and leads to better agreement with experiment. Finally, we reemphasize that use of the pair 11-*cis*, 12-*s-cis* and 11-*cis*, 12-*s-trans* to explain the observed temperature dependence requires that 11-*cis*, 12-*s-trans* be the more stable rotamer, in disagreement with the calculations and with the crystal geometry; however, it is not impossible that the calculations are in error or that the crystal and solution geometries are a consequence of secondary interactions.<sup>30</sup>

The second effect, that involving the variation of Franck-Condon overlap integrals, arises from the change in the population of the vibrational levels of the ground electronic state as a function of temperature. Although for an electronic transition moment independent of geometry the total intensity from all of the thermally populated vibrational levels of the ground state to all of the levels of the excited state is independent of temperature as a consequence of the vibrational sum rule,<sup>32</sup> a significant shift of intensity can occur due to the variation of Franck-Condon integrals for different ground state levels. This can give the appearance of a decrease in the intensity of a given vibronically unresolved electronic transition and an increase in that of other bands.

The intensities of transitions from excited vibrational levels of the electronic ground state can be evaluated in the harmonic approximation by the use of recursion formulae.<sup>19</sup> This was done for 11-*cis*,12-*s-cis*-retinal and the spectrum at 77 and 300°K was constructed from the results (Figure 14). Although the lines become broader at higher temperature, the observed thermal effect is not reproduced. However, as already pointed out in section II, the calculated potential surface is "shallower" than that obtained from the harmonic approximation. More important, intermolec-

(32) G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, Princeton, N. J., 1950, p 203.

ular effects that can significantly modify the potential have not been taken into account.

We have demonstrated in section II (e.g., Figure 13) that the shape, position, and structure of the  $\pi\pi^*$  absorption is very sensitive in 11-*cis*,12-*s-cis*-retinal to the value of the angle  $\phi_{12-13}$  in the ground state and to the concomitant change in this angle on excitation. Further, we have seen that a way of reproducing the observed diffuse spectrum is by assuming that, as a result of medium perturbations, a range of  $\phi_{12-13}$  angles is occupied by molecules in the ground state. If, in addition, there were a significant change in the range of  $\phi_{12-13}$  angles as a function of temperature, a thermal effect on the  $\pi\pi^*$  transition would result. Experiments<sup>8,19,26</sup> show that upon warming the height of the peak is sharply reduced while the peak becomes broader and significant intensity is shifted to fill in the region at 5000–10000  $\text{cm}^{-1}$  higher frequency. The observed behavior is reproduced if the vibronic mapping (described at the end of section II) is done for 70°K by superposition of calculated conformations with  $\phi_{12-13}$  ranging from  $-25$  to  $-40^\circ$  and a maximum probability at  $-35^\circ$ , while the observed structure at 300°K is represented by contributions from conformations with  $\phi_{12-13}$  between  $-30$  and  $-45^\circ$  and a maximum probability at  $-40^\circ$ . Furthermore, even if the average angle stayed unchanged but sufficient conformations were populated on both sides of the equilibrium point, the asymmetry of the vibronic envelopes with respect to shift from the minimum might account for the observed effect. It should be noted, however, that the thermal shift of the  $\phi_{12-13}$  equilibrium angle for the *calculated* potential is less than  $2^\circ$  and that the minimum is somewhat too deep to allow sufficient thermal population of neighboring conformations to give the experimental results. Thus, small modifications in the potential to correct for inaccuracies in the calculations and/or medium effects would be required to give the described thermal redistribution of the low-frequency modes in the electronic ground state.

The thermal modification of the vibronic structure at *all-trans*-retinal was examined by a corresponding approach. The calculation indicated that the electronic line shape is not significantly affected by conformational changes in the neighborhood of the minimum energy geometry. Moreover, in *all-trans*-retinal the minima for twisting around chain single bonds are much less shallow than that of the 12–13 bond in 11-*cis*,12-*s-cis*-retinal.

#### IV. Concluding Discussion

In this work we have used a semiempirical technique developed for conjugated molecules to study the vibronic structure of the strongly allowed  $\pi\pi^*$  transition of  $\beta$ -ionone and certain retinal isomers. A series of model calculations were made to examine the origin of the diffuse absorption spectrum in all of these molecules and the source of the strong temperature dependence in 11-*cis*-retinal. It appears probable from our results that the dominant factor in the diffuse spectrum is the

large change on excitation of the 6–7 torsional angle between the cyclohexane ring and the polyene chain. It was shown that if the change in torsional angles upon excitation is somewhat larger than that corresponding to the calculated potential the diffuseness can be attributed completely to the torsional progressions and their coupling with other modes. However, the broad nature of the ground state potential suggests that a slightly varying local environment for different molecules may be responsible for a significant portion of the observed diffuseness.

As to the temperature dependence of the 11-*cis* spectrum, the origin is somewhat less clear. The present calculations demonstrate that one possibility is a change with temperature in the effective average value of the torsional angle  $\phi_{12-13}$  in the ground state of 11-*cis*,12-*s-cis*-retinal. This could be due to the anharmonicity in the torsional motion or to alterations of the medium interactions with temperature, both of which could play an important role because of the broad and flat nature of the potential. An alternative possibility is that the equilibrium between two conformations (e.g., 11-*cis*, 12-*s-trans* and 11-*cis*, 12-*s-cis*) is involved in the observed thermal effect. It would be most helpful here to have additional data for these various retinal isomers and suitably modified molecules (e.g., temperature dependence of the spectrum of isomers with critical methyl groups such as 5 or 13 removed);<sup>33</sup> low-temperature spectra in dilute single crystals would also be of great interest.

It is evident that the primary importance of the theoretical methods employed in this paper is that they provide a technique for determining the vibronic structure of the electronic transition from the ground and excited state potential surfaces involved. There is no longer any need to introduce doubtful simplifying approximations which focus on only a single bond and exclude all other effects of the potential surfaces. However, it must be cautioned that calculating potential surfaces, particularly for large sterically hindered molecules, of sufficient accuracy to completely predict the vibronic structure of electronic transitions is not yet feasible. Instead, as we have tried to demonstrate, the semiempirical surfaces serve best as a first approximation which can be utilized with appropriate adjustments for exploring possible explanations of observed phenomena (e.g., diffuseness of unresolved spectra, relative intensities in resolved spectra).

The work described in this paper was concerned only with the strongly allowed  $\pi\pi^*$  transition of retinal and related molecules. The overlap integrals between various vibrational levels of other electronic surfaces can also be estimated by the present method. Such integrals, as well as other nonadiabatic coupling terms which can be evaluated by the same techniques, will allow a detailed study of the photoisomerization process of these molecules.

(33) R. Nelson, J. K. de Riel, and A. Kropf, *Proc. Nat. Acad. Sci. U. S.*, **66**, 531 (1970).