

## THE ELECTRONIC STRUCTURE OF C-NITROSO-COMPOUNDS

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**Abstract**—The electronic absorption spectra of nitroso-methane, nitroso-ethylene and nitroso-benzene were investigated by the PPP and CNDO/2 method. The unusual energy level spacing may lead to an interesting photophysical behaviour making fluorescence from the second excited singlet state of aromatic nitroso-compounds conceivable. The source of intensity of the forbidden low-frequency transition at 13 kK in nitroso-benzene is also discussed.

### INTRODUCTION

A striking feature of monomeric nitroso-compounds is the occurrence of a very longwave  $n \rightarrow \pi^*$  transition ( $S_1 \leftarrow S_0$ ) and an unusually large energy gap between the first ( $S_1$ ) and the second ( $S_2$ ) excited singlet state. The aim of this investigation is a comparative study of the spectral properties of nitroso-alkanes, nitroso-alkenes and aromatic nitroso-compounds. Current quantum chemical methods correctly describe the experimental findings. The electronic structure, spectroscopy and theoretical aspects of C-nitroso-compounds have been previously reviewed by Gowenlock and Lüttke,<sup>1</sup> Rao and Bhaskar<sup>2</sup> and Wagnière.<sup>3</sup> The blue colour of the aliphatic nitroso-alkanes results from a low intensity absorption ( $\epsilon \sim 1$ – $100 \text{ mol}^{-1} \cdot \text{l} \cdot \text{cm}^{-1}$ ) in the 16–12 kK region. Further absorption maxima occur around 36 ( $\epsilon \sim 100$ ) and 45 kK ( $\epsilon \sim 5000$ ). Aromatic nitroso-compounds are green and have weak absorption ( $\epsilon \sim 50$ ) in the 15–13 kK range. Stronger bands are observed above 33 kK. The nitroso-alkenes are not stable at room temperature and polymerize easily. It is interesting to note that already Lewis and Kasha<sup>4</sup> have studied the unusual colour of nitroso-compounds in one of their early papers. Their assignment of the long wavelength band to a  $T_1 \leftarrow S_0$  transition proved, however, to be incorrect. Further aspects of the spectroscopy of the nitroso-group have been treated by other authors.<sup>5–11</sup>

A basically correct interpretation of the electronic spectrum of nitroso-methane was given by McEwen<sup>12</sup> using a simplified MO-model. A CNDO calculation with configuration interaction has been reported by Kuhn *et al.*<sup>13</sup> It confirmed the assignment of McEwen but overestimated the oscillator strength of the  $n \rightarrow \pi^*$  transition. An *ab initio* calculation of the electronic spectrum of nitroso-methane using large configuration interaction was performed by Ha and Wild.<sup>14</sup> The calculated singlet spectrum  $n \rightarrow \pi^*$ : 17.5 kK,  $f = 1.18 \times 10^{-3}$ ,  $n \rightarrow \pi^*$ : 57.6 kK,  $f = 4.83 \times 10^{-3}$  and  $\pi \rightarrow \pi^*$ : 87.8 kK,  $f = 0.632$  is in agreement with experimental data.

In this paper the electronic absorption spectra of nitroso-methane (1), of *cis*- and *trans*-nitroso-ethylene (2a,b), and of nitroso-benzene (3), using both the PPP and the CNDO/2 method, will be investigated and compared.

### EXPERIMENTAL

To illustrate the unusual electronic spectra of nitroso-compounds the absorption spectrum of nitroso-benzene is given in Fig. 1. Spectra of  $10^{-2}$ ,  $10^{-3}$ ,  $10^{-4}$  and  $10^{-5}$  molar EtOH solns were recorded on a computer controlled spectrophotometer and used to calculate the molar absorption coefficients.<sup>15,16</sup> The absorption maxima and oscillator strengths are reported in Table 3.

### CALCULATIONS

(a) *Structures* (Fig. 2). Coffey *et al.*<sup>17</sup> determined the structure of nitroso-methane by microwave spectroscopy. In the electronic ground state the eclipsed form is preferred. *Ab initio* calculations<sup>18</sup> support this assignment and lead to a barrier of rotation of approx. 4 kJ/mol.

For nitroso-ethylene itself no structural data are available. Recently Nösberger *et al.*<sup>19</sup> reported an improved structure of nitro-ethylene which was used for the  $\text{CH}_2 = \text{CH} - \text{N}$  part of the molecule, whereas the same N–O bond distance was assumed as for nitroso-methane.

In the case of nitroso-benzene the structural parameters of Hanyu and Boggs<sup>20</sup> were employed.

(b) *PPP calculation with configuration interaction*. For the PPP calculations the parameterization reported by Labhart and Wagnière<sup>10</sup> was used with the exception that all  $\gamma$ -integrals were calculated applying the Nishimoto-Mataga approximation.<sup>21</sup>

(c) *CNDO/2 with configuration interaction*. For the CNDO calculations the program CNDUV80 was used.

This program was developed by one of the authors (H.B.) and evolved from the QCPE program 100. The SCF process was improved by the extrapolation method proposed by Hartree.<sup>22</sup> The program was optimized with respect to computing speed and memory space. The parameters were those of del Bene *et al.*<sup>23</sup> The transition

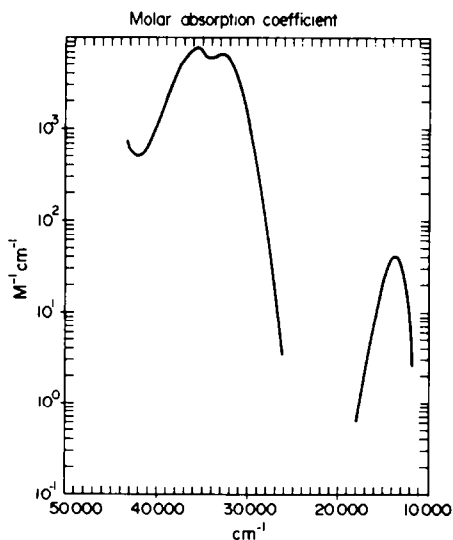


Fig. 1. Absorption spectrum of nitroso-benzene in ethanol at room temperature.

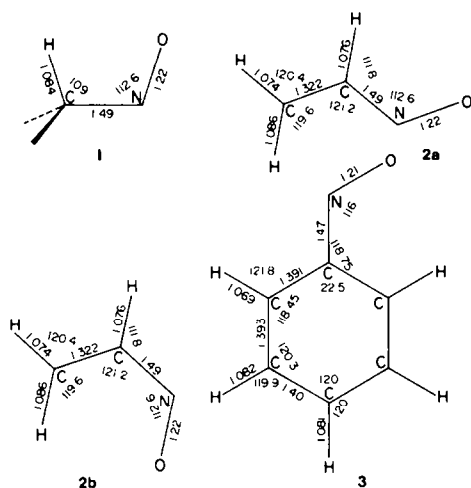


Fig. 2. Geometry of nitroso-methane (1), *trans*- and *cis*-nitroso-ethylene (2a,b), and nitroso-benzene (3) (bond lengths in Å, bond angles in degrees).

moments were calculated using the approximation by Ellis *et al.*<sup>24</sup> which gives nonvanishing values for  $n-\pi^*$  transitions in planar conjugated systems. All configurations having an energy below 80 kK (below 120 kK for nitroso-methane) were considered in the configuration interaction treatment.

## RESULTS AND DISCUSSION

(a) *PPP calculations on nitroso-ethylene and nitroso-benzene.* In order to characterize some general properties of nitroso-compounds it is instructive to split the  $\pi$ -system into two parts: the nitroso-group and the remaining part of the  $\pi$ -system. The molecules nitroso-ethylene and nitroso-benzene are thus discussed with the help of the  $\pi$ -system of nitroso-methane and of ethylene or benzene, respectively. The orbital energy diagrams (Fig. 3) and the LCAO representation of corresponding MO's indicate clearly that a classification in terms of the separated systems is still meaningful. The ground state of the nitroso-ethylenes is represented by  $[(N\pi)^2(E\pi)^2]$  where  $N\pi$  and  $E\pi$  describe MO's predominantly

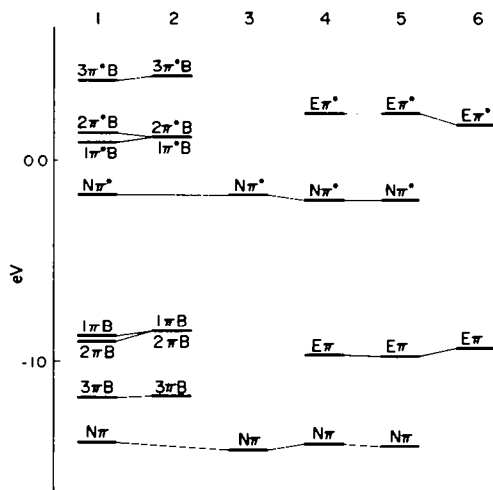


Fig. 3. Molecular orbital energies from PPP calculations. (1) Nitroso-benzene; (2) Benzene; (3) Nitroso-methane; (4) *cis*-Nitroso-ethylene; (5) *trans*-Nitroso-ethylene; (6) Ethylene.

Table 1. Nitroso-methane. Singlet- and triplet-state energies

state	symmetry	ab initio <sup>a)</sup>		CNDO/2			PPP		experiment <sup>d)</sup>	
		energy kK	f	energy kK	f <sup>b)</sup>	f <sup>c)</sup>	energy kK	f	energy kK	log $\epsilon_{\max}$
S <sub>1</sub>	A''	17.51	0.0012	12.36	0.0003	0.0193	77.6	0.618	14.44	1.38
S <sub>2</sub>	A''	57.85	0.0048	51.92	0.0017	0.0079			14.86	1.33
S <sub>3</sub>	A'	87.77	0.632	76.01	0.318	0.192				
S <sub>4</sub>	A'			80.35	0.049	0.048				
S <sub>5</sub>	A''			80.41	0.002					
T <sub>1</sub>	A''	10.41		12.36			21.5			
T <sub>2</sub>	A'	43.49		33.35						
T <sub>3</sub>	A''	65.11		51.92						
T <sub>4</sub>	A'			76.67						
T <sub>5</sub>	A''			80.41						

a) see ref. 14

b) transition moments in dipole-vector form; approximations see text.

c) transition moments in dipole-velocity form; see ref. 25.

d) see ref. 7, CF<sub>3</sub>NO.

localized in the nitroso- and in the ethylene-group, respectively. The ground state of nitroso-benzene is given by  $[(N\pi)^2(3B\pi)^2(2B\pi)^2(1B\pi)^2]$  where the  $B\pi$ -orbitals are of the benzene type.

For nitroso-ethylene four singly excited configurations can be defined:  $E\pi \rightarrow N\pi^*$ ,  $E\pi \rightarrow E\pi^*$ ,  $N\pi \rightarrow N\pi^*$  and  $N\pi \rightarrow E\pi^*$ . A representation of the results of the corresponding singlet configuration interaction treatment is given in Table 2. It is evident that the transition near 41 kK has a dominant contribution of the  $E\pi \rightarrow N\pi^*$  configuration which promotes an electron from the ethylene part into the nitroso-group. The internal charge transfer character of this band is further demonstrated by the calculated charge densities in the excited state. In *cis*-0.53 and in *trans*-nitroso-ethylene 0.59 electron charges are transferred from the ethylene- to the nitroso-part.

The results for nitroso-benzene are summarized in Table 3. The  $\pi$ -system involves 8 centers and 8 electrons

and allows the construction of 16 singly excited configurations. The first two singlet states occur at 30.83 and at 32.95 kK and result predominantly from the promotion of an electron in a benzene orbital to a nitroso-group orbital  $1B\pi \rightarrow N\pi^*$  which is also indicated by the large internal charge transfer. The next two states correlate with the two lowest states in benzene. The perturbation by the nitroso-group introduces, however, significant oscillator strength into these bands. The agreement between the calculated and the observed transitions is very good for all four bands. The PPP method therefore describes excellently the  $\pi \rightarrow \pi^*$  transitions of nitroso-benzene.

(b) *CNDO/2 calculations.* As in the previous section the behaviour of the  $\pi$ -orbitals has been treated with the PPP approach, we concentrate in this part on the  $n$ - and  $\sigma$ -orbitals and on the transitions which include these orbitals.

1. *Nitroso-methane.* Let us first compare the results of

Table 2. *Cis*- and *trans*-nitroso-ethylene. Singlet state energies

state	CNDO/2				PPP					
	config. description <sup>a)</sup>		energy kK	f	config. description <sup>a)</sup>		energy kK	f	charge density	
	config.	coeff.			config.	coeff.			N	O
$S_0$ cis									0.06	-0.26
$S_0$ trans									0.06	-0.24
$S_1$ cis	$n_- \rightarrow 1\pi^*$	0.89	11.32	0.0003						
$S_1$ trans	$n_- \rightarrow 1\pi^*$	0.87	11.72	0.0002						
$S_2$ cis	$n_- \rightarrow 2\pi^*$	0.87	48.06	0.0001						
$S_2$ trans	$n_- \rightarrow 2\pi^*$	0.84	48.51	0.002						
$S_3$ cis	$1\pi \rightarrow 1\pi^*$	0.87	48.45	0.1405	$E\pi \rightarrow N\pi^*$	0.99	40.81	0.543	-0.33	-0.40
$S_3$ trans	$1\pi \rightarrow 1\pi^*$	0.95	51.34	0.314	$E\pi \rightarrow N\pi^*$	0.98	42.03	0.893	-0.34	-0.43
$S_7$ cis					$E\pi \rightarrow E\pi^*$	0.80	67.92	0.047	0.05	0.00
$S_7$ trans					$E\pi \rightarrow E\pi^*$	0.88	69.24	0.352	0.03	0.03
$S_{10}$ cis					$N\pi \rightarrow N\pi^*$	0.80	75.65	0.779	0.06	-0.15
$S_{10}$ trans					$N\pi \rightarrow N\pi^*$	0.89	73.69	0.054	0.11	-0.15

<sup>a)</sup> only the main component is listed

Table 3. Nitroso-benzene. Singlet state energies

state	CNDO/2				PPP						experiment <sup>b)</sup>	
	config. description <sup>a)</sup>		energy kK	f	config. description <sup>a)</sup>		energy kK	f	charge density		energy kK	$\log \epsilon_{\max}$
	config.	coeff.			config.	coeff.			N	O		
$S_0$									0.08	-0.21		
$S_1$	$n_- \rightarrow 1\pi^*$ $n_- \rightarrow 3\pi^*$	0.77 0.60	11.26	0.0003							13.15	1.64
$S_2$	$2\pi \rightarrow 1\pi^*$ $1\pi \rightarrow 2\pi^*$	0.73 0.62	36.65	0.003	$1B\pi \rightarrow N\pi^*$	0.95	30.83	0.045	-0.29	-0.53	33.18	3.72
$S_3$			42.70	0.182	$2B\pi \rightarrow N\pi^*$	0.96	32.93	0.461	-0.35	-0.50	35.65	4.01
$S_6$			49.57	0.162	$2B\pi \rightarrow 1B\pi^*$	0.73	44.48	0.025	-0.03	-0.24	45.87	3.81
$S_8$			51.09	0.236	$N\pi \rightarrow 1B\pi^*$	0.82	51.45	0.169			51.54	4.08

<sup>a)</sup> only the main component is listed.

<sup>b)</sup> ref. 9 and this work.

the CNDO/2 treatment with the *ab initio* calculation of Ha *et al.*<sup>14</sup> In Fig. 4 corresponding molecular orbital levels are shown. It is satisfying to note that both methods lead to the same sequence and to good numerical agreement of the occupied orbitals as well as for the singlet and triplet state energies (Table 1). Both calculations predict a low lying  $A''$  singlet state as expected for nitroso-alkanes and a large gap of about 40 kK to the second singlet state which has the same symmetry. In terms of orbital promotion the transition  $S_1 \leftarrow S_0$  corresponds to an almost pure promotion of an electron from the antibonding combination of the lone pair orbitals of nitrogen and oxygen to the antibonding  $\pi^*$ -orbital  $1a''$ . The second transition  $S_2 \leftarrow S_0$  results mostly from the promotion of an electron from the bonding combination of the lone pair orbitals to the same  $1a''$ -orbital. The third transition is of  $\pi \rightarrow \pi^*$  ( $1a'' \rightarrow 1a''$ ) type and is strongly allowed. The oscillator strengths from the two calculated transitions show about the same relative behaviour, the *ab initio* value being 2–3 times larger.

*Ab initio* calculations of the optical spectra of larger nitroso systems would involve a substantial increase in computer time. In view of the good agreement mentioned above it seems certain that the CNDO/2 approximation is

adequate to discuss the optical spectra of the larger nitroso-compounds.

2. *Nitroso-benzene*. The two highest occupied and the four lowest unoccupied orbitals are of  $\pi$ -symmetry. Nevertheless, the low frequency transition at 11.23 kK results from a promotion of an electron from the  $n$ -orbital to a combination of the  $1\pi^*$ - and the  $3\pi^*$ -orbitals. As in nitroso-methane and in the nitroso-ethylenes this  $n$ -orbital represents an antibonding combination of the  $n$ -orbitals of N and O. All the other orbitals of  $a'$ -symmetry form the  $\sigma$ -core and the corresponding  $\sigma \rightarrow \pi^*$ -transitions lie at much higher energies. The next two transitions at 36.65 and 42.7 kK are of  $\pi \rightarrow \pi^*$ -origin. The transition to the singlet states  $S_4$  and  $S_5$  again involve promotions from the  $n$ - to the  $\pi^*$ -orbitals and are buried under the stronger  $\pi \rightarrow \pi^*$ -transitions.

On account of the ZDO approximation, the CNDO method predicts zero singlet-triplet splitting for configurations of  $n \rightarrow \pi^*$ -type. The observed splitting in keto-compounds is indeed small and seldom exceeds 2 kK. The calculated singlet-triplet splitting between configurations of  $\pi \rightarrow \pi^*$ -type is large and seven triplet states of  $\pi \rightarrow \pi^*$  origin at 20.4, 29.4, 29.8, 36.6, 36.7, 42.0 and 44.2 kK are predicted to lie between the first and the second triplet state of  $n \rightarrow \pi^*$ -origin.

The large energy gap of 25 kK between  $S_2$  and  $S_1$  will inhibit efficient internal conversion and raises the possibility of fluorescence from  $S_2$ . In addition, the generally efficient intersystem crossing from the  $^1\pi \rightarrow \pi^*(S_2)$ - to a  $^3n \rightarrow \pi^*(T_1)$ -state will be small due to the large energy gap. However, intersystem crossing from  $S_2$  to the four triplet states ( $T_3, T_4, T_5, T_6$ ) of  $^3\pi \rightarrow \pi^*$ -type, which lie in the interval  $S_2 + 0.2$  kK to  $S_2 - 10$  kK, may be efficient. One would therefore expect that the  $S_2$  state of nitroso-benzene will behave just like an  $S_1$  state of an aromatic hydrocarbon and a rather detailed balance between the efficiencies of the radiative properties of  $S_2$  and the intersystem crossing probabilities to  $T_3 - T_6$  will decide the feasibility of  $S_2$  luminescence. The most favorable conditions for such a luminescence might exist in substituted nitroso-benzenes where  $S_2$  has a larger oscillator strength.

The electronic absorption spectrum of nitroso-benzene in the 13 kK region has been investigated by Bhujle *et al.*<sup>11</sup> The torsional levels show a spacing of about  $100\text{ cm}^{-1}$  in the ground and of  $50\text{ cm}^{-1}$  in the first excited singlet state. Let us consider the origin of its oscillator strength in more detail.

If the N–O chromophore has a local  $C_{2v}$  symmetry such as the model system  $H_2NO^+$ , group theory will predict zero oscillator strength for the electric dipole transition from  $S_0$  to  $S_1$ . The calculated singlet state energies, the oscillator strengths, and the symmetry classifications of the four lowest transitions in  $H_2NO^+$  are given in Table 4.

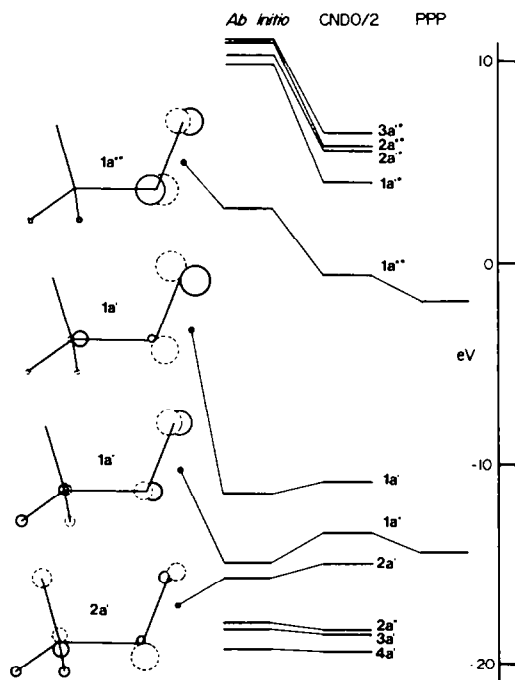


Fig. 4. Molecular orbital energies of nitroso-methane.

Table 4. Singlet-state energies, oscillator strengths, and symmetry classification of  $H_2NO^+$

CNDO/2			$C_{2v}$		$C_s$	
state energy kK	oscillator strength	orbital transition	symmetry	polarization	symmetry	polarization
14.33	0	$n \rightarrow 1\pi^*$	$b_1 \otimes b_2 = A_2$	forbidden	$a' \otimes a'' = A''$	y
69.59	0.010	$2\pi \rightarrow 1\pi^*$	$a_1 \otimes b_2 = B_2$	y	$a' \otimes a'' = A''$	y
86.51	0.336	$1\pi \rightarrow 1\pi^*$	$b_2 \otimes b_2 = A_1$	z	$a'' \otimes a'' = A'$	x, z
94.94	0.058	$n \rightarrow 1\sigma^*$	$b_1 \otimes a_1 = B_1$	x	$a' \otimes a' = A'$	x, z

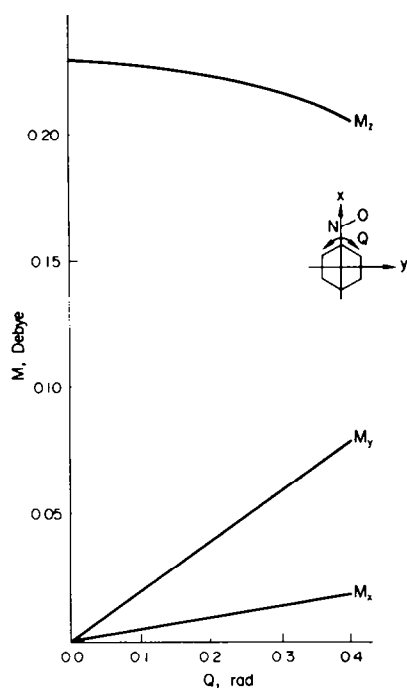


Fig. 5. Components of the electronic transition dipole moment of the 11.3 kK transition in nitroso-benzene.

$$\mathbf{M}_{\text{ef}}(\mathbf{Q}) = \left\langle \Psi_e(\mathbf{q}; \mathbf{Q}) \left| \sum_{i=1}^n e_i \mathbf{r}_i \right| \Psi_f(\mathbf{q}; \mathbf{Q}) \right\rangle.$$

Table 5. Calculated oscillator strength  $f_{v,w}$  between torsional levels ( $\times 10^6$ )

$$f_{v,w} = \frac{8\pi^2 m \cdot c \cdot \tilde{\nu}_{\text{ef}}}{3 \cdot h \cdot e^2} |\mathbf{M}_{\text{ef},v,w}|^2$$

The integrals of type

$$\langle \chi_{\text{ev}}(\mathbf{Q}) | \mathbf{M}_{\text{ef}}(\mathbf{Q}) | \chi_{\text{fw}}(\mathbf{Q}) \rangle$$

with

$$\begin{aligned} \mathbf{M}_{\text{ef}}(\mathbf{Q}) &= \mathbf{M}_{\text{ef}}(\mathbf{Q}_0) + \left( \frac{\partial}{\partial \mathbf{Q}} \mathbf{M}_{\text{ef}} \right)_{\mathbf{Q}_0} (\mathbf{Q} - \mathbf{Q}_0) \\ &+ \frac{1}{2} \left( \frac{\partial^2}{\partial \mathbf{Q}^2} \mathbf{M}_{\text{ef}} \right)_{\mathbf{Q}_0} (\mathbf{Q} - \mathbf{Q}_0)^2 \end{aligned}$$

where  $\mathbf{Q}$  represents the torsional angle were estimated by calculating the overlap integrals between undisplaced but distorted harmonic oscillators. Rather severe approximations have been introduced in calculating  $\mathbf{M}_{\text{ef}}(\mathbf{Q})$  and not more than an order of magnitude agreement with the experimental results can be expected.

$v \leftarrow w$	0 (25 $\text{cm}^{-1}$ )	1 (75 $\text{cm}^{-1}$ )	2 (125 $\text{cm}^{-1}$ )
0 (50 $\text{cm}^{-1}$ )	245	6	17
1 (150 $\text{cm}^{-1}$ )	13	195	6
2 (250 $\text{cm}^{-1}$ )	8	30	136

Lowering of the local symmetry of the N=O chromophore to  $C_s$ , such as in nitroso-benzene, will make the transition to  $S_1$  allowed with a polarization perpendicular to the molecular plane. Even though formally allowed, it will still have very low oscillator strength.

The intensity distribution of the vibrational structure can be obtained, as is well known, by considering the transition dipole moment:

$$\mathbf{M}_{\text{ef},v,w} = \langle \chi_{\text{ev}}(\mathbf{Q}) | \mathbf{M}_{\text{ef}}(\mathbf{Q}) | \chi_{\text{fw}}(\mathbf{Q}) \rangle$$

with

$$\mathbf{M}_{\text{ef}}(\mathbf{Q}) = \langle \Psi_e(\mathbf{q}; \mathbf{Q}) \left| \sum_{i=1}^n e_i \mathbf{r}_i \right| \Psi_f(\mathbf{q}; \mathbf{Q}) \rangle$$

where  $\Psi_e(\mathbf{q}; \mathbf{Q})$  and  $\Psi_f(\mathbf{q}; \mathbf{Q})$  are the electronic and  $\chi_{\text{ev}}(\mathbf{Q})$  and  $\chi_{\text{fw}}(\mathbf{Q})$  the vibrational wave functions. The electronically allowed transitions with  $\mathbf{M}_{\text{ef}}(\mathbf{Q}_0)$  evaluated at the planar equilibrium configuration would suggest that only transitions between vibrational levels of the same parity would occur. The transition moment  $\mathbf{M}_{\text{ef}}(\mathbf{Q})$  depends, however, as shown in Fig. 5, markedly on the angle of an out-of-plane displacement of the NO-group. The NO torsional motion will, as shown in Table 5 and observed in the related case of keto-compounds,<sup>26,27</sup> introduce significant oscillator strength in the electronically forbidden transitions between vibrational levels of opposite parity.

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