

# On the photoelectron spectrum of the NO dimer, and the ground state of $(\text{NO})_2^+$

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The vibrational structure of the photoelectron spectrum of the NO dimer is calculated by *ab initio* methods, and compared with the observed ZEKE (zero electron kinetic energy) spectra published by I. Fischer *et al.* [J. Chem. Phys. **96**, 7171 (1992)] and A. Strobel *et al.* [J. Phys. Chem. **99**, 872 (1995)]. The ground state potential of  $(\text{NO})_2^+$  is calculated to have almost iso-energetic minima at planar cis ( $C_{2v}$ ) and trans ( $C_{2h}$ ) geometries, but the Franck–Condon factors from the ground state of  $(\text{NO})_2$  strongly favor transitions to the cis isomer. The good agreement for the vibrational frequencies and intensities shows that the  $(\text{NO})_2^+$  isomer reached in the photoelectron spectrum has a cis-planar  $C_{2v}$  structure, rather than the twisted  $C_2$  structure proposed by Fischer *et al.*, or the trans-planar  $C_{2h}$  structure proposed by A. Strobel *et al.* © 1999 American Institute of Physics. [S0021-9606(99)01713-4]

The thermodynamic properties<sup>1</sup> of the open-shell gas nitric oxide show the presence of dimers that are relatively well bound compared to typical van der Waals molecules. A recent measurement<sup>2</sup> gives  $D_0^0 = 764 \text{ cm}^{-1}$  for these dimers. The vibrational and rotational spectra of the dimers have been studied extensively by various techniques in the solid, liquid, gas, rare-gas matrix, and molecular beam phases. (See Ref. 3 for references.) However, recent assignments of the intermolecular vibrations in the gas phase<sup>3</sup> from far-infrared and hot-band measurements, supported by *ab initio* calculations,<sup>3,4</sup> suggest that the relationship between the vibrational frequencies in the gas phase and in condensed phases is still not well understood.

On ionization, the NO dimer produces a cation  $(\text{NO})_2^+$  with a much larger dissociation energy ( $D_0^0 = 4956 \text{ cm}^{-1}$ , by combining the data of Refs. 2 and 5). This has been studied<sup>5</sup> with a resolution of the order of  $1 \text{ cm}^{-1}$  by a two-photon ZEKE (zero electron kinetic energy) technique, although the bands had a width of about  $7 \text{ cm}^{-1}$ , probably due to unresolved rotational structure.<sup>5</sup> The vibrational structure in this photoelectron spectrum was initially interpreted<sup>5</sup> in terms of a nonplanar cis structure of the cation, in contrast to the planar cis  $C_{2v}$  structure of the neutral species. This interpretation was later changed<sup>6</sup> to that of a planar trans  $C_{2h}$  structure for the cation. However, a possible alternative assignment of this vibrational structure in terms of a planar cis  $C_{2v}$  cation was suggested previously,<sup>7</sup> in the context of the reconsideration of the intermolecular vibrations of the neutral species. The present article presents a more detailed consideration of this reassignment with the assistance of new *ab initio* calculations.

For the ground electronic state of the cation  $(\text{NO})_2^+$  we have used MOLPRO96<sup>8</sup> to calculate points on the torsional potential with open-shell coupled-cluster RCCSD(T) theory<sup>9</sup> and the aug-cc-pVDZ basis set.<sup>10</sup> The results show that there are essentially iso-energetic energy minima at the trans-

planar  $C_{2h}$  and cis-planar  $C_{2v}$  structures. The  $C_{2h}$  structure is actually found to be lower than the  $C_{2v}$  structure by  $70 \text{ cm}^{-1}$ , but this is well within the accuracy of the method. The structure with dihedral angle  $\tau = 90^\circ$  was found to be  $517 \text{ cm}^{-1}$  above the  $C_{2h}$  structure. The optimized geometries at these three torsional angles are given in Table I. The energies give the approximate torsional potential (relative to the cis structure at  $\tau = 0$ )

$$V(\tau)/\text{cm}^{-1} = -35(1 - \cos \tau) + 241(1 - \cos 2\tau).$$

To examine the implications of these results for the ZEKE spectrum, we have calculated one-dimensional torsional Franck–Condon factors between the ground states of the neutral and cation dimer, using a program adapted from that for the  $V-N$  transition of ethylene.<sup>11</sup> The ground state torsional potential of the neutral was taken as

$$V(\tau)/\text{cm}^{-1} = 1209.5(1 - \cos \tau) + 910.9(1 - \cos 2\tau),$$

based on previous *ab initio* calculations,<sup>4</sup> and the coefficient of  $p_\tau^2$  was taken as constant at the cis value for the neutral and at the mean of the values for the cis and trans geometries for the cation. The squares of the calculated Franck–Condon factors are shown on a logarithmic scale in Fig. 1. It is clear that at low torsional energies the spectrum will have a strong branch to the states that are predominantly cis and an extremely weak branch to the states that are predominantly trans. The trans spectrum, with a torsional progression with rapidly rising intensities, is completely inconsistent with the observed ZEKE spectrum.<sup>5,6</sup> On the other hand, the calculated cis spectrum, with a ratio of 11.5 in intensity between the 0–0 and 2–0 torsional bands is consistent with the observed ZEKE spectrum, assuming that the principal observed structure is due to totally symmetric vibrations,<sup>7</sup> and that the torsional bands are weak, as calculated. Thus we conclude that the cis and trans geometries are approximately iso-

TABLE I. Structures of  $(\text{NO})_2$  and  $(\text{NO})_2^+$  ( $r$  in Å,  $\theta$  in deg).

	$r(\text{NO})$	$r(\text{NN})$	$\theta(\text{NNO})$
$(\text{NO})_2$ <i>ab initio</i>	1.1692	2.2273	96.25
$(\text{NO})_2$ spectrum <sup>a</sup>	1.1515	2.2630	97.17
$(\text{NO})_2^+$ <i>ab initio</i> cis	1.1226	2.2956	102.12
$(\text{NO})_2^+$ <i>ab initio</i> $\tau=90^\circ$	1.1225	2.3000	114.38
$(\text{NO})_2^+$ <i>ab initio</i> trans	1.1216	2.2739	111.91
$(\text{NO})_2^+ - (\text{NO})_2$ cis <i>ab initio</i>	-0.0466	0.0683	5.87
$(\text{NO})_2^+ - (\text{NO})_2$ cis fit 1	-0.0383	0.1233	3.03
$(\text{NO})_2^+ - (\text{NO})_2$ cis fit 2	-0.0345	-0.0923	7.88

<sup>a</sup>Reference 7.

energetic, but because of Franck–Condon propensities the observed ZEKE spectrum can be regarded as going purely to the cis isomer.

For a more detailed study of the ZEKE intensities we have optimized the harmonic force field of  $(\text{NO})_2^+$  in its ground  $^2A_1$  state with the same *ab initio* methods. The harmonic force field was determined with energies and coordinate transformations obtained using the MOLPRO96<sup>8</sup> and INTDER94<sup>12</sup> codes, respectively. In essence, the very same procedure was used for the cation as for the ground  $^1A_1$  state of the neutral,<sup>3</sup> and a very similar cis-planar  $C_{2v}$  geometry was located. The only difference is that the  $b_2$  force constants of the cation fall victim to a symmetry-breaking phenomenon.<sup>13</sup> The  $b_2$  frequencies are not needed to match any significant feature of the ZEKE spectrum, and so are not discussed further here. The structure of the ion at this minimum is calculated to be strictly cis-planar, and so, as shown above, the progression in the  $a_2$  torsional vibration, calculated to have a harmonic frequency of  $151 \text{ cm}^{-1}$ , is expected to be weak. (Note that this frequency is much higher than the value of about  $91 \text{ cm}^{-1}$  calculated from the torsional potential above; in the latter the geometry was optimized at each torsional angle, and so partial effects of anharmonicity are included.) The band near  $35\,387 \text{ cm}^{-1}$  in the ZEKE spec-

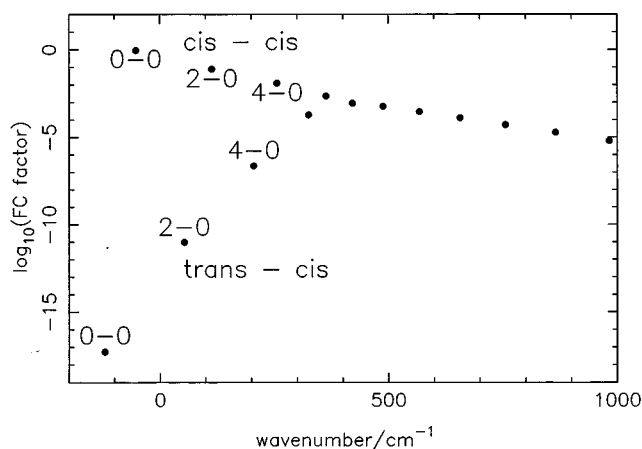


FIG. 1. Calculated one-dimensional torsional Franck–Condon factors from the ground electronic state of  $(\text{NO})_2$  to the ground electronic state of  $(\text{NO})_2^+$ . The wavenumber scale is relative to the separation between the cis minima. At low energies, the stronger transitions go to levels with wavefunctions localized near the cis minimum of the cation potential and the much weaker ones to levels with wavefunctions localized near the trans minimum of the potential.

TABLE II.  $a_1$  harmonic potential constants<sup>a,b</sup> and frequencies<sup>c</sup> of  $(\text{NO})_2$  and  $(\text{NO})_2^+$ .

	$(\text{NO})_2$ calculated	$(\text{NO})_2^+$ calculated <sup>d</sup>	$(\text{NO})_2^+$ observed <sup>e</sup>
$F_{11}=f_R$	0.3577	0.5284	
$F_{22}=f_r+f_{rr}$	15.2646	19.4602	
$F_{33}=f_\alpha+f_{\alpha\alpha}$	0.7730	0.1770	
$F_{12}=\sqrt{2}f_{Rr}$	0.0714	0.1160	
$F_{13}=\sqrt{2}f_{R\alpha}$	0.3291	0.1225	
$F_{23}=f_{r\alpha}+f_{r\alpha'}$	-0.1788	-0.0283	
$\omega_1$	1862.4	2102.0	2090
$\omega_2$	278.9	324.3	323
$\omega_3$	200.8	123.4	118

<sup>a</sup>The symmetry coordinates are  $S_1=\delta R$ ,  $S_2=(\delta r+\delta r')/\sqrt{2}$ ,  $S_3=(\delta\alpha+\delta\alpha')/\sqrt{2}$ .<sup>b</sup>Units:  $\text{aJ}/\text{\AA}^2$  for stretch–stretch,  $\text{aJ}/\text{rad}\text{\AA}$  for stretch–bend, and  $\text{aJ}/\text{rad}^2$  for bend–bend.<sup>c</sup>Units:  $\text{cm}^{-1}$ .<sup>d</sup>Cis isomer.<sup>e</sup>ZEKE values from Ref. 5. Present assignments.

trum of Fig. 2 of Ref. 6 appears to be of about the correct wavenumber and relative intensity to be the 2–0 torsional transition; this assignment would give a torsional fundamental of about  $126 \text{ cm}^{-1}$  in the cation.

The *ab initio*  $a_1$ -species force constants of the neutral and the cation are presented in Table II. The *ab initio*  $a_1$  vibrational frequencies are very close to the intervals observed in the photoelectron spectrum,<sup>5,6</sup> confirming the interpretation as a  $C_{2v}-C_{2v}$  transition with progressions in the three totally symmetric modes, as proposed previously.<sup>7</sup>

We use the *ab initio* results in Tables I and II in calculations of harmonic Franck–Condon factors. For transitions that preserve  $C_{2v}$  symmetry there is no problem of rotation of the Eckart axes (“axis-switching”<sup>14</sup>) and the transformation between the dimensionless normal coordinates of the neutral ( $q_l''$ ) and ion ( $q_k'$ ) states is

$$q_k' = \delta_k + \sum_l D_{kl} q_l'' \quad (1)$$

where<sup>15</sup>

$$\delta_k = (hc\omega_k'/\hbar^2)^{1/2} \sum_{i\alpha} m_i^{1/2} l'_{iak} [(r_{i\alpha}^e)'' - (r_{i\alpha}^e)'] \quad (2)$$

$$\mathbf{D} = (\omega')^{1/2} (\mathbf{I}')^T (\mathbf{I}'') (\omega'')^{-1/2} \quad (3)$$

Here  $r_{i\alpha}^e$  are the equilibrium coordinates of the atoms and  $\mathbf{I}$  are the transformation matrices between mass-weighted Cartesian displacements and normal coordinates. The *ab initio* parameters in Tables I and II give the values

$$\delta = \begin{bmatrix} -1.241 \\ -0.539 \\ 1.590 \end{bmatrix}, \quad \mathbf{D} = \begin{bmatrix} 1.056 & 0.309 & 0.024 \\ -0.034 & 0.714 & 0.946 \\ -0.020 & 0.493 & -0.523 \end{bmatrix} \quad (4)$$

The matrix  $\mathbf{D}$  includes the effect of the Dushinskiĭ rotation of normal coordinates,<sup>16</sup> which is seen to be large for the  $q_2$  and  $q_3$  modes.

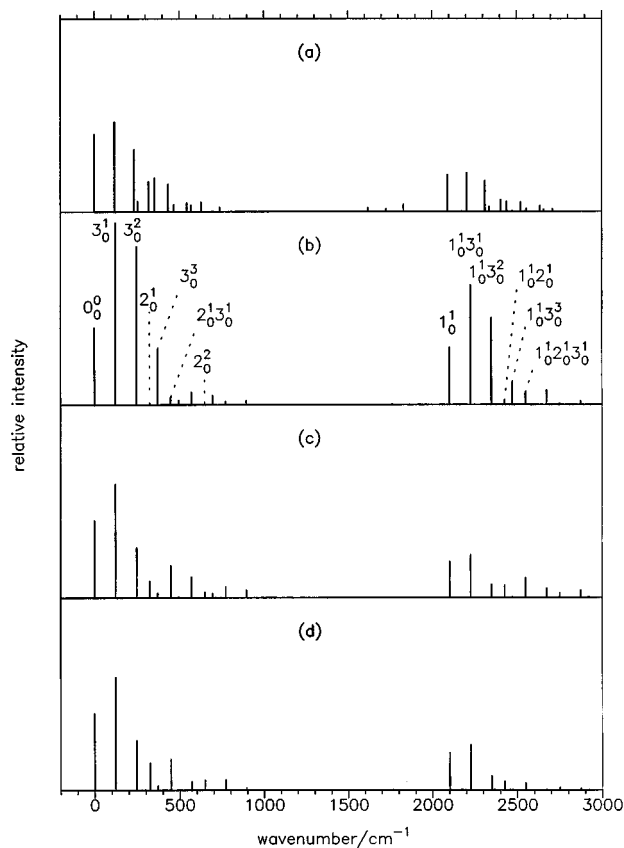


FIG. 2. Observed and calculated relative vibrational intensities in the ZEKE spectrum of  $(\text{NO})_2$ . (a) Observed stick spectrum based on Fig. 2 of Ref. 6. (b)–(d) Relative Franck–Condon factors calculated from the *ab initio* geometries of  $(\text{NO})_2$  and: (b) the *ab initio* geometry of  $(\text{NO})_2^+$ , (c) the fit 1 geometry of  $(\text{NO})_2^+$ , and (d) the fit 2 geometry of  $(\text{NO})_2^+$ . (See Table I.) The spectra are normalized so that the  $0_0^0$  band has the same intensity in each panel.

Following the method of Sharp and Rosenstock<sup>17,18</sup> the generating function for the Franck–Condon integrals  $\langle v'_1 v'_2 v'_3 | 000 \rangle$  from the neutral zero-point level is obtained as

$$\exp\left\{\frac{1}{2}\tilde{\mathbf{s}}(\mathbf{E}-\mathbf{B}^{-1})\mathbf{s} + (1/\sqrt{2})\tilde{\mathbf{s}}\mathbf{B}^{-1}\boldsymbol{\delta}\right\} = \sum_{v'_1 v'_2 v'_3} \frac{\langle v'_1 v'_2 v'_3 | 000 \rangle s_1^{v'_1} s_2^{v'_2} s_3^{v'_3}}{\langle 000 | 000 \rangle (v'_1! v'_2! v'_3!)^{1/2}}, \quad (5)$$

where

$$\mathbf{B} = \frac{1}{2}(\mathbf{E} + \mathbf{D}\mathbf{D}^T), \quad (6)$$

and  $\mathbf{E}$  is the unit matrix. For the low quantum numbers considered here, the integrals can be computed by expanding the left side of Eq. (5) and picking out the terms with the correct powers of the generating variables  $s_1$ ,  $s_2$ , and  $s_3$ .

The photoelectron spectrum calculated using the squares of these Franck–Condon integrals is shown in Fig. 2(b), compared with the observed relative intensities in Fig. 2(a). It is seen that the qualitative pattern of intensities is well calculated, and this leaves little doubt that the photoelectron spectrum corresponds to a  $C_{2v} - C_{2v}$  transition with a relatively minor change in geometry.

The ion normal coordinates  $q'_3$ ,  $q'_2$ , and  $q'_1$  are found to correspond fairly accurately to OO, NN, and symmetric NO stretching motions, respectively. The observed intensities in the  $\nu_3$  progression suggests that the increase in OO distance is slightly exaggerated in the *ab initio* calculation, while the  $\nu_1$  intensities imply that the decrease in the NO distance is well predicted. The main disagreement is in the  $\nu_2$  progression, which is much stronger in the observed spectrum than predicted. In this case there is a near-cancellation between terms in the Franck–Condon calculation, which is therefore sensitive to small errors in either the calculated change of geometry or the calculated force constants (or both). For example, the increase in NN distance may be underestimated by the *ab initio* calculation. A fit of the observed intensities adjusting the  $\delta_k$  parameters allowing for a larger increase in  $r(\text{NN})$  is shown in Fig. 2(c). There is a notable improvement, and the resulting geometrical parameters are shown as fit 1 in Table I. However, a slightly better fit is obtained by assuming that  $r(\text{NN})$  decreases on ionization. The result is shown in Fig. 2(d), with the geometrical parameters given as fit 2 in Table I.

Comparisons of the *ab initio*  $\nu_2$  and  $\nu_3$  results with experiment<sup>3,5,6</sup> suggest that RCCSD(T)<sup>9</sup> predicts the neutral dimer to be slightly too strongly bound and the cation dimer to be slightly too weakly bound. Therefore it is not inconceivable that fit 2 is the more appropriate of the two fits, as these tendencies suggest that the intermonomer distances should be longer for the neutral and shorter for the cation than are currently predicted. However, these considerations are given mainly to indicate that slight changes in the parameters can remove the near-cancellation of the  $2_0^1$  intensity. At the moment it is not possible to say whether the geometries or the force constants are at fault.

In summary, *ab initio* calculations have shown that the two-photon ZEKE photoelectron spectrum<sup>5,6</sup> of  $(\text{NO})_2$  can be understood in terms of transitions to the  $C_{2v}$  cis minimum of the ground-state potential of the ion  $(\text{NO})_2^+$ . Transitions to the  $C_{2h}$  trans minimum, which is almost iso-energetic, have extremely small Franck–Condon factors, and are not observed. The *ab initio* vibrational frequencies are in very good agreement with this assignment, which is also supported by calculated Franck–Condon factors. The main discrepancy is in the intensity of transitions to  $\nu'_2$  and to combination levels involving  $\nu'_2$ . Clearly further *ab initio* work or a rotationally resolved photoelectron spectrum would help to resolve this relatively minor discrepancy.

We are grateful to a referee for a suggestion that caused us to explore the trans minimum of the cation potential, which will be important in other experiments such as matrix isolation spectra.

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- <sup>13</sup>Symmetry breaking is an occasional problem in molecular-orbital-based methods and refers to the existence of multiple solutions of the Hartree–Fock equations that have lower symmetry than that of the nuclear framework, although the exact solutions for the true Hamiltonian are not expected to have lower symmetry. For  $(\text{NO})_2^+$ , as for  $\text{HCO}_2$  (Ref. 19) or  $\text{LiO}_2$  (Ref. 20), the alternative solutions to the Hartree–Fock equations are two equivalent broken-symmetry solutions in which the last (odd) electron is localized on one or the other side of the molecule. If the solutions lie close enough in energy, the usual symmetry-constrained delocalized solution will be adversely affected in *some* (but not all) ways; most notably in its vibrational force constants for motions which make the two sides of the molecule inequivalent. This problem has also been observed for the  $b_{3u}$  vibration of the quite similar dioxygen dimer cation (Refs. 21–23). See Refs. 19–23 for further discussions of symmetry breaking.
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