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On the Spectroscopically Determined Potential Energy Surfaces for the Electronic Ground States of NO_2 and H_2O

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Previous spectroscopically determined potentials for both $H_2{}^{16}O$ and NO_2 are discussed. It is shown that a recent $H_2{}^{16}O$ potential energy surface due to D. Xie and G. Yan (1996. *Chem. Phys. Lett.* **248,** 409), which was determined by fits to vibrational term values alone and was claimed to be more accurate than other published spectroscopically determined potentials for this system, actually gives unacceptably poor results for rotationally excited water. Reasons for this failure are discussed and the dangers of relying on vibrational term values alone are emphasized. Previous spectroscopic potentials for ground state NO_2 are all found to have problems with unphysical minima (''holes''). Starting from the potential energy surface for the ground ($\tilde{X}\,{}^2A_1$) electronic state of NO_2 constructed by S. A. Tashkun and P. Jensen (1994. *J. Mol. Spectrosc.* **165,** 173) using the approximate MORBID approach a suitable starting point for fits using an exact kinetic energy operator approach was constructed. Least-squares fits to 17 potential parameters gives a potential which reproduces 173 vibrational term values with a standard deviation of only 2.8 cm^{-1} in the low-energy region ($<$10 000 cm^{-1}). For many even levels below, and all levels above, approximately 10 000 cm^{-1} the first excited electronic state ($\tilde{A}\,{}^2B_2$) perturbs the vibrational energy levels of the ground state. We were unable to fit these levels. Tests show that the resulting effective potential surface has no problems with unphysical holes and gives a reasonable representation of the rotational structure of the low-lying vibrational states of NO_2.

I. INTRODUCTION

In recent years there has been increasing use of variational calculations to invert spectroscopic data and obtain spectroscopically determined (effective) potential energy surfaces. Indeed for light triatomic molecules this method is rapidly taking over from perturbation theory as the method of choice for representing experimental data. A particular virtue of this method is that for a given system the vibrations and rotations are governed by the same potential. This means that data obtained on vibrationally excited levels can help to determine the behavior of the molecule under rotational excitation and vice versa.

In this paper we discuss spectroscopically determined potentials for the systems NO_2 and $H_2{}^{16}O$. The water molecule both is of fundamental importance and has become a testing ground for various inversion techniques. In part this is because conventional, perturbation theory based, effective Hamiltonians diverge when used to represent higher rotationally excited states of water. A number of water potentials have been determined using spectroscopic data. Recent surfaces include those due to Jensen (*1*), Jensen *et al.* (*2*), Paulse and Tennyson (*3*), Polyansky *et al.* (PJT) (*4, 5*), Xie and Yan (XY) (*6*), and Partridge and Schwenke (*7*).

There are several reasons for attempting to create an accurate ground electronic state potential energy surface for NO_2. There is a full set of vibrational energy levels available (*8*). The problem is interesting as quantum chaos sets in at higher energies (*9–11*). Also, a ground state PES is needed to study the problems involved with the coupling with the higher electronic state and to study the breakdown of the Born–Oppenheimer approximation. There is additional interest in NO_2 as it is an atmospherically important molecule, notably being involved in atmospheric ozone chemistry (*12*).

There have been several previous spectroscopic determinations of the NO_2 $\tilde{X}\,{}^2A_1$ state potential. The first attempt was by Tashkun and Jensen (TJ) (*13*). This potential has been subsequently refined by Vilanove and Jacon (VJ) (*14*) and Xie and Yan (*15*), with XY claiming significantly higher accuracy. These potentials will be discussed in the next section. The ground and first excited potential energy surfaces of NO_2 have also been the subject of a series of *ab initio* studies by Petrongolo and co-workers (*16–21*). The most recent of these works (*20, 21*) also uses available experimental data to refine their potential, but the accuracy achieved was significantly lower than the other determinations discussed above.

II. PREVIOUS POTENTIALS

(a) H_2O

Recently Xie and Yan (*6*) presented a new spectroscopically determined potential energy surface for $H_2{}^{16}O$. This

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surface was determined using variational calculations and the available observed vibrational term values up to 21 221 cm^{-1}. It reproduced these term values with a standard deviation of only 1.1 cm^{-1}, better than any then available spectroscopic potential. No rotational data was used in this fit and no rotational analysis was undertaken.

We have programmed the potential given by XY. This potential has no problems with unphysical minima, ‘‘holes,’’ and we reproduced their vibrational calculations with minor differences below 10 000 cm^{-1}. However, calculations using XY’s surface show that it performs very poorly for rotationally excited states of $H_2{}^{16}O$. Table 1 compares term values for levels with moderate rotational excitation, $J = 10$, for the ground and bending fundamental states. The calculations presented were performed with the exact kinetic energy (EKE) program suite DVR3D (*22*) and basis sets documented elsewhere (*4*). Parallel calculations performed with the approximate kinetic energy MORBID program (*23*) gave very similar results.

Table 1 shows that for states with low K_a, which are usually relatively easy to fit, the XY potential behaves poorly giving errors ∼3 cm^{-1}. For the more difficult high K_a states the XY potential gives completely unacceptable errors of between 28 and 90 cm^{-1}.

For comparison Table 1 also gives the results obtained using the recently spectroscopically determined PJT2 potential of Polyansky *et al.* (*5*). This potential was determined using not only 63 vibrational term values but also 3200 rotational term values with excitation up to $J = 14$. It is clear that the PJT2 potential gives an excellent representation of the rotationally excited states. Similar agreement was obtained with Polyansky *et al.*’s previous spectroscopically determined potential (*4*). Furthermore we have demonstrated that these potentials are capable of very accurate extrapolation; for rotational states up to as high as they have been assigned experimentally, $J \sim 35$, errors of only ∼0.1 cm^{-1} are found (*4*).

So why is it that XY’s calculation gives such poor results for rotationally excited water? The answer lies in the fact that vibrational term values alone are insufficient to characterize a potential energy surface. In the case of harmonic oscillations it is immediately apparent that the vibrational energies are independent of the equilibrium geometry chosen. Similarly for anharmonic potentials one can model the vibrational energy levels of a molecule with a surface based about an incorrect equilibrium geometry. Thus, for example, in the case of water it is possible to model the bending vibrational term values of water with a number of different combinations of pure bending potential parameters, f_0^2, f_0^3, $\cdots$ (see below). However, the different combinations will give very different behavior for rotationally excited states, particularly those with high K_a. Thus parameters which give excellent results for the vibrational term values can easily give a distorted potential which does not reproduce the rotational energy level structure of the molecule. This is what appears to have happened in this case.

There are two factors which seem to have contributed to the problem with XY’s potential. First, XY chose to fix their $H_2{}^{16}O$ equilibrium geometry at the values used by Jensen (*1*) who in turn used an *ab initio* value for the equilibrium bond angle. It is well established that this angle is too small (*2, 3*); the difference is only ∼0.1°, but this is sufficient to significantly affect the rotational levels of the molecule (*2, 3*).

The second problem concerns the data actually used in XY’s fit. While many water stretching overtone and combination bands have been observed, there is very little experimental data available for vibrational levels with significant bending excitation. Only bending overtones up to $4\nu_2$ had been directly observed. However, the rotational levels of the bands $(v_1v_2v_3) = (130)$ and (220) are observed to be significantly perturbed and ‘‘dark’’ state analysis has produced estimates of the vibrational term values for the bending overtones (050) (*24*) and (070) (*25*). XY included the estimate of the (050) term value and that for (060) (*26*). Our recent analysis (*5*) suggests that the dark state vibrational term values are in error, probably because the rotational structure of the dark states is insufficiently well characterized to allow for extrapolation back to the $J = 0$ level. Indeed recent assignment of the spectrum of hot water has confirmed this suspicion in the case of (050) (*29*). Our analysis also shows that the (060) term value, whose derivation appears obscure, is also incorrect.

It would be simplistic to dismiss problems with XY’s spectroscopically determined potential as due to a poor equilibrium structure or the inclusion of unreliable data. The error in the equilibrium structure is very small and the higher bending overtones characterize potential parameters which otherwise would remain ill-determined. The fundamental problem is that vibrational term values alone are insufficient to correctly characterize a spectroscopically determined potential. This is demonstrated by Fernley *et al.* (*30*) who compared four spectroscopically characterized water potentials and found that the use of even modest rotational data, levels with $J \leqslant 2$, led to a significant improvement in the resulting potential.

(*b*) NO_2

Subsequent to their work on water, Xie and Yan (*6*) also presented a potential for NO_2. This potential started from that of Tashkun and Jensen (*13*), from which we also start; see below. TJ originally performed their fits using vibrational term values up to 9500 cm^{-1} and rotational data for a few low-lying states and the MORBID program (*23*). MORBID is based on the use of an approximate kinetic

TABLE 1

Comparison of Rotational Term Values with $J = 10$, in cm^{-1}, for $H_2{}^{16}O$ for the Ground Vibrational State and ν_2 States

			Ground vibrational state			(010) vibrational state		
J	K_a	K_c	Observed(27)	PJT2	XY	Observed(28)	PJT2	XY
10	0	10	1114.53242	0.041	2.9	2705.097	−0.00	2.4
10	1	10	1114.55005	0.042	2.9	2705.097	−0.05	2.4
10	1	9	1293.01830	0.061	2.9	2903.147	0.00	2.6
10	2	9	1293.63420	0.060	2.1	2904.429	−0.01	3.1
10	2	8	1437.96866	0.092	0.7	3058.400	0.03	−0.7
10	3	8	1446.12847	0.076	3.1	3072.728	−0.01	3.6
10	3	7	1538.14967	0.129	3.6	3162.259	0.05	−5.6
10	4	7	1581.33627	0.079	4.6	3224.548	−0.02	6.9
10	4	6	1616.45318	0.120	0.9	3253.739	0.01	−0.7
10	5	6	1718.71904	0.061	9.9	3383.266	−0.08	15.4
10	5	5	1724.70566	0.072	7.7	3387.402	−0.07	13.2
10	6	5	1874.97326	0.031	18.1	3564.705	−0.13	26.2
10	6	4	1875.46195	0.031	17.8	3565.004	−0.13	26.5
10	7	4	2054.34548	−0.002	28.0	3770.713	−0.16	40.2
10	7	3	2054.36894	−0.001	28.0	3770.728	−0.16	40.2
10	8	3	2254.28407	−0.033	39.1	3997.511	−0.17	55.1
10	8	2	2254.28455	−0.033	39.1	3997.511	−0.17	55.1
10	9	2	2471.25531	−0.066	61.6	4240.942	−0.14	71.5
10	9	1	2471.25531	−0.066	61.6	4240.942	−0.14	71.5
10	10	1	2701.88936	−0.100	65.4	4497.198	−0.04	89.4
10	10	0	2701.88936	−0.100	65.4	4497.198	−0.04	89.4

Note. The calculations used the potential of Polyansky *et al.* (PJT2) (*5*) and Xie and Yan (XY) (*6*). Calculated term values are shown as observed minus calculated.

energy operator, and experience has shown (*4, 30*) that this leads to small errors in potentials determined using it.

XY refined TJ's potential by fitting to the 142 vibrational term values which lie 9000 cm^{-1} or less above the ground state. In doing this XY claim that their surface reduces the weighted error for these states from 14.3 to 2.1 cm^{-1}. XY did not allow for the fact that some of the vibrational states in their fit might be perturbed by the other low-lying electronic states in the NO_2 system.

Vilanove and Jacon (*14*) also performed a modest refine-

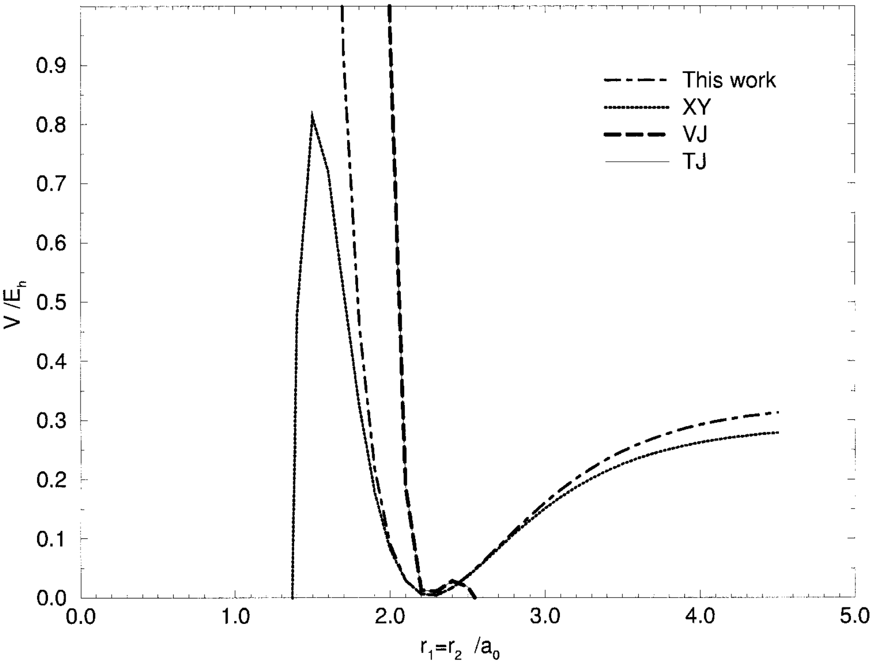

FIG. 1. Comparison of spectroscopically determined NO_2 ground state potentials. The cut is for the symmetric stretching mode with bond lengths r_1 and r_2 frozen equal, and the bond angle $\theta = 2.2$ rad. The Tashkun and Jensen (TJ) (*13*) and Vilanove and Jacon (VJ) (*14*) potentials are very similar but have a severe unphysical minimum at bonglengths only slightly larger than equilibrium. Xie and Yan's (XY) (*15*) potential has an unphysical minimum at short bond lengths. Our potential is well behaved throughout the region.

ment of TJ's potential using vibrational term values up to 7000 cm^{-1}. VJ's potential reproduces their data with an error of 9.8 cm^{-1}.

We have attempted to test XY's surface but have been unable to perform sensible variational calculations on it as published because of the presence of deep unphysical minima, holes. The less serious of these holes occurs when one bond length is compressed below 0.7 Å. A more serious and extensive hole occurs in the symmetric stretch, its closest approach to equilibrium being $r \sim 1.06$ Å where $\theta \sim 115°$. Figure 1 gives a cut through XY's potential chosen to illustrate the effect of this hole. As can be seen from this plot, both the TJ and the VJ potentials suffered even more seriously from problems with holes.

For tests on the XY potential, we removed the effects of the unphysical minima by flattening the potential over the regions where they occurred. That is, in the regions where holes were evident we gave the potential the same value as that near the top of the barrier into the holes. Removal of the holes from the TJ potential is harder and will be discussed further below.

Finally, Leonardi *et al.* (LPHB) (*20*) refined their *ab initio* calculations (*17*) to obtain potential energy surfaces for NO_2, not only for the $\tilde{X}\,^2A_1$ electronic ground state but also for the $\tilde{A}\,^2B_2$ low-lying excited state plus the surface which couples them. Despite adjusting 87 coefficients in their potentials, LPHB only reproduced the low-lying vibrational term values of the system with a standard deviation of 17.8 cm^{-1}. Like XY, LPHB did not consider rotational excitation; however, a major thrust of their work was the vibronic structure of the system in the region, above 10 000 cm^{-1}, where the two electronic states are strongly coupled.

It is notable that although TJ used rotational data to help them determine their potential, all the subsequent calculations considered only vibrational term values. In view of the experience with water discussed above, such an approach must be viewed with caution. In particular, VJ chose to vary the parameter $f_1^{(0)}$ (see below) which TJ had fixed as zero. $f_1^{(0)}$ fixes the first derivative of the potential with respect to stretching coordinates at the expansion point. Resetting from zero has the effect of shifting the equilibrium geometry of the potential. Performing such a shift without reference to rotational data must be regarded as particularly dangerous. We note that very recently VJ performed comparisons, but not fits, with rotational data (*31*).

III. A NEW FITTED POTENTIAL FOR NO_2

(*a*) *The Potential Energy Function*

The potential energy function used in this work has the analytical form originally given by Jensen (*1*),

$$\begin{aligned} V(\Delta r_1, \Delta r_3, \bar{\rho}) = V_0(\bar{\rho}) &+ \sum_j F_j(\bar{\rho}) y_j \\ &+ \sum_{j \leqslant k} F_{jk}(\bar{\rho}) y_j y_k + \sum_{j \leqslant k \leqslant m} F_{jkm}(\bar{\rho}) y_j y_k y_m \\ &+ \sum_{j \leqslant k \leqslant m \leqslant n} F_{jkmn}(\bar{\rho}) y_j y_k y_m y_n, \end{aligned} \tag*{[1]}$$

where all of the indices j, k, m, and n assume the values 1 or 3. The quantity y_j in Eq. [1] is given by

$$y_j = 1 - \exp(-a_j \Delta r_j), \tag*{[2]}$$

where the a_j are molecular constants and $\Delta r_j = r_j - r_j^e$, $j =$ 1 or 3, is defined as a displacement from the equilibrium value r_j^e of the distance r_j between the ''outer'' nucleus $j =$ 1 or 3 and the ''center'' nucleus 2. The quantity $\bar{\rho}$ is the instantaneous value of the bond angle supplement. The $F_{jkm\cdots}$ expansion coefficients of Eq. [1] are functions of $\bar{\rho}$ and defined as

$$F_j(\bar{\rho}) = \sum_{i=1}^{4} f_j^{(i)} (\cos \rho_e - \cos \bar{\rho})^i, \tag*{[3]}$$

and

$$F_{jk\cdots}(\bar{\rho}) = f_{jk\cdots}^{(0)} + \sum_{i=1}^{N} f_{jk\cdots}^{(i)} (\cos \rho_e - \cos \bar{\rho})^i, \tag*{[4]}$$

where ρ_e is the equilibrium value of $\bar{\rho}$ and the $f_{jk\cdots}^{(i)}$ are expansion coefficients. The function $F_{jk}(\bar{\rho})$ has $N = 3$, $F_{jkl}(\bar{\rho})$ has $N = 2$, and $F_{jklm}(\bar{\rho})$ has $N = 1$. The function $V_0(\bar{\rho})$ is the potential energy for the molecule bending with bond lengths fixed at their equilibrium values, and here we parameterize it as

$$V_0(\bar{\rho}) = \sum_{i=2}^{8} f_0^{(i)} (\cos \rho_e - \cos \bar{\rho})^i, \tag*{[5]}$$

where the $f_0^{(i)}$ are expansion coefficients.

(b) Experimental Data

The vibrational term values used here were obtained by Delon and Jost (*8*) using laser induced dispersed fluorescence spectroscopy of jet cooled NO_2. They recorded the complete set of 191 vibrational levels below 10 000 cm^{-1} and some levels up to 12 000 cm^{-1}. The first electronically excited state lies at about 9734 cm^{-1} above the vibrational ground state (*8, 20*).

Data on the rotationally excited states is available for a number of low-lying vibrational states (*32, 33*). However, our calculations do not consider spin interaction effects and so we have used the deperturbed rotational data calculated by Kozin (*34*) for TJ. This data consists of rotational term values with $N \leqslant 5$ for the (0, 0, 0), (0, 1, 0), (1, 0, 0), (0, 2, 0), and (0, 0, 1) vibrational states.

(c) Calculations

Calculations of the vibrational terms were performed using the EKE DVR3D program (*22*). For these calculations we used Radau coordinates with a dense angular grid of 115 DVR points based on Gauss–Legendre quadrature. For the radial coordinates grids were generated using Morse oscillator-like functions (*22*) specified by the parameters (r_e, D_e, ω_e) = (2.81, 1.3, 0.007) in atomic units. DVR grids with 37 point Gauss–Laguerre quadrature points in each coordinates were symmetrized by taking combinations of actual grid points. The dimension of the final Hamiltonian used to calculate the band origins was 1800.

Rotational calculations were performed using the ROTLEV3B program which is part of the DVR3D suite. ROTLEV3B performs the second step of a two-step variational calculation for the rovibrational states of triatomic molecules. Tests on both the vibrational and rotational steps of the calculation suggested that the basis sets used were actually somewhat larger than was required to obtain adequate convergence of the energy levels.

The derivatives of the potential constants with respect to changes in the energy levels were calculated using the Hellman–Feynman theorem. A new module, XPECT3, was written to perform this task within a DVR framework.

We attempted to use the original surface of TJ for EKE calculations of the band origins of NO_2. These calculations failed due to the presence of holes in certain areas of the potential. Analysis of TJ's potential suggested that these holes were caused by the large negative values of the parameters $f_{13}^{(3)}$ and $f_{1113}^{(1)}$.

Therefore, these parameters were reset to zero and a new fit, using the MORBID program, was attempted. There is of course a discrepancy between energy levels calculated using MORBID and those using an EKE operator. It has been noted previously (*4*) that the discrepancy is essentially constant with respect to changes in the potential parameters. Thus it was possible to use the corrected MORBID levels for fitting once the correction factor had been determined. Using this technique a potential was constructed which had a similar standard deviation to TJ's but no spurious minima in physically important regions. This new potential was used as the starting point for fits using the EKE operator.

A least-squares fitting procedure was then implemented to find the optimum values for the potential parameters. These fits used a mixture of the sophisticated Interactive Non-Linear Least Squares (I-NoLLS) (*35*) program suite and a simpler minimization procedure.

(d) Removal of Poorly Fitted Levels

We initially tried to determine the potential using all 114 even levels and 77 odd levels below 10 000 cm^{-1}. Fitting of the NO_2 surface is complicated by the intersection between the ground electronic state and the first excited state which is at approximately 10 000 cm^{-1}. The interaction between these two states perturbs the energy levels of the ground state. During the fitting procedure we removed several levels from the fit as they appeared not to be improving. It was assumed that this was because of the interactions with the higher state, although, in a single surface calculation, we had no direct evidence for this.

Many of the states removed, which are labeled in Tables 3 and 4, have the common feature that they have a large value for v_2. It is also notable that in the region covered by XY's calculations, the levels we removed are those which are systematically too low in their calculation. Above about 9500 cm^{-1}, many even levels were removed. It is clear from LPHB's calculation (see Fig. III of Ref. (*20*)) that nearly all states in this region are strongly perturbed by vibronic interactions. Conversely we found it unnecessary to remove any odd states below 9500 cm^{-1} and only the (4, 0, 3) and (0.11, 1) levels above this. The work of LPHB shows that the energies of the lower odd states are much less sensitive to vibronic effects than the corresponding even states and that the (4, 0, 3) state is indeed the first to be strongly perturbed. Conversely the recent study of Leonardi and Petrongolo (*21*) shows that odd states above 10 000 cm^{-1} are perturbed more strongly than even ones.

(e) Adding of Additional Potential Parameters

The constants that were initially fitted were $f_0^{(2)}$, $f_0^{(3)}$, $f_0^{(4)}$, $f_1^{(1)}$, $f_1^{(2)}$, $f_{11}^{(0)}$, $f_{11}^{(1)}$, $f_{13}^{(0)}$, $f_{111}^{(1)}$, $f_{113}^{(1)}$, and $f_{1113}^{(0)}$. We reached the limit of the improvements that could be made by fitting these parameters. However, these constants were well determined and the correlation between them was very low; we therefore investigated whether the potential could be improved by allowing more higher order constants in the potential to float during the fit.

We were able to determine the additional constants $f_1^{(3)}$, $f_{11}^{(2)}$, $f_{13}^{(1)}$, $f_{13}^{(2)}$, $f_{113}^{(0)}$, and $f_{1113}^{(1)}$. Of these 17 potential parameters, $f_{111}^{(1)}$ was found to be very poorly determined so it was discarded from the list of parameters that we tried to fit. We also tried to fit $f_0^{(5)}$, $f_{111}^{(0)}$, and $f_{1111}^{(0)}$ but found that we could not determine meaningful values for them.

Final values for the optimized potential constants are given in Table 2.

TABLE 2
Nonzero NO_2 Potential Parameters Determined in Our Final Least-Squares Fit

Parameter	Value /cm^{-1}	Error /cm^{-1}
$f_0^{(2)}$	78259.20740	51
$f_0^{(3)}$	−107129.99582	358
$f_0^{(4)}$	225437.38541	307
$f_1^{(1)}$	−9514.44438	107
$f_1^{(2)}$	−33493.10799	467
$f_1^{(3)}$	−3080.26035	325
$f_{11}^{(0)}$	27019.00973	14
$f_{11}^{(1)}$	16052.75505	271
$f_{11}^{(2)}$	652.42584	236
$f_{13}^{(0)}$	9106.89156	40
$f_{13}^{(1)}$	1094.98984	570
$f_{13}^{(2)}$	7446.65832	802
$f_{113}^{(0)}$	−410.29378	142
$f_{113}^{(1)}$	−1567.88852	514
$f_{1113}^{(0)}$	4507.28671	26
$f_{1113}^{(1)}$	−1841.45757	159
ρ_ϵ /°	46.233	
r_1^ϵ / Å	1.18724	
a_1 /$Å^{-1}$	3.1848	

(f) Levels above 10 000 cm^{-1}

After fitting the potential as optimally as possible to the data available up to 10 000 cm^{-1}, we tried to fit it to the available data up to 12 000 cm^{-1}. Even when we removed the levels with the worst agreement we were unable to make any significant reduction in the standard deviation. We believe that this problem stems from the interaction of the ground state with higher electronic states.

(g) Comparison with Experimental Data

The initial standard deviation of the fit was 8.0 cm^{-1}. The final standard deviation achieved after fitting, and after the levels listed were removed, was 2.8 cm^{-1}.

As mentioned above, the experimental data we used for fitting and comparison purposes was that of Delon and Jost (*8*). For a comparison of our calculated vibrational term values with those of Delon and Jost see Tables 3 and 4.

We used our optimized potential to calculate rovibrational levels up to $N = 5$. We used the vibrational and rotational term quoted by Tashkun and Jensen (*13*) for

TABLE 3
Observed Even Symmetry Vibrational Term Values (8) and Observed Minus Calculated Values (cm^{-1})

(ν_1,ν_2,ν_3)	Obs	O−C	(ν_1,ν_2,ν_3)	Obs	O−C	(ν_1,ν_2,ν_3)	Obs	O−C
0,1,0	749.64	−0.24	5,0,0	6475.05	2.18	5,3,0	8623.34	3.55
1,0,0	1319.79	−1.85	1,7,0	6497.60	0.58	2,0,4	8652.27	−1.87
0,2,0	1498.34	0.22	1,3,2	6616.53	1.29	1,10,0	8690.72	7.98*
1,1,0	2063.12	−2.39	4,2,0	6653.54	−0.53	1,6,2	8758.28	−0.26
0,3,0	2246.04	0.98	0,9,0	6705.23	−0.72	4,5,0	8809.81	4.12
2,0,0	2627.34	−2.70	0,5,2	6823.80	0.45	4,1,2	8817.61	−0.36
1,2,0	2805.60	−2.37	3,4,0	6837.75	−2.36	1,2,4	8868.35	−0.82
0,4,0	2993.00	2.05	3,0,2	6921.67	2.41	0,12,0	8911.29	−4.89
0,0,2	3201.44	−4.17	0,1,4	6979.21	−3.78	7,0,0	8968.55	8.78*
2,1,0	3364.57	−3.10	2,6,0	7029.48	−0.09	0,8,2	8982.08	0.81
1,3,0	3547.10	−1.95	2,2,2	7125.60	3.11	3,7,0	9003.53	9.70*
0,5,0	3738.60	2.68	5,1,0	7193.35	2.84	3,3,2	9031.81	0.57
3,0,0	3922.61	−1.98	1,8,0	7231.06	2.32	0,4,4	9082.71	−2.32
0,1,2	3929.12	−2.92	1,4,2	7332.45	1.19	6,2,0	9151.35	8.21
2,2,0	4100.58	−3.46	4,3,0	7374.57	−0.40	2,9,0	9203.99	15.59*
1,4,0	4286.82	−1.84	0,10,0	7443.09	−1.92	0,0,6	9226.23	−3.78
1,0,2	4461.07	0.53	1,0,4	7478.02	1.24	2,5,2	9247.78	−0.84
0,6,0	4482.57	2.55	0,6,2	7544.62	0.65	5,0,2	9295.48	−8.76*
3,1,0	4652.00	−2.16	3,5,0	7562.47	0.18	5,4,0	9334.06	5.25
0,2,2	4656.34	−1.95	3,1,2	7627.14	3.08	2,1,4	9341.17	−4.85
2,3,0	4835.05	−3.77	0,2,4	7681.49	−3.16	1,11,0	9416.05	12.66*
1,5,0	5025.20	−1.47	6,0,0	7730.08	5.63	1,7,2	9468.38	−0.71
1,1,2	5180.54	0.84	2,7,0	7757.29	3.63	4,2,2	9511.96	0.30*
4,0,0	5205.81	−0.42	2,3,2	7834.97	2.00	4,6,0	9524.14	8.94
0,7,0	5224.55	1.38	5,2,0	7909.46	2.89	1,3,4	9561.06	−3.26
0,3,2	5377.91	−1.07	1,9,0	7962.27	4.73	0,13,0	9640.29	−6.60
3,2,0	5384.41	−2.47	1,5,2	8046.44	0.64	7,1,0	9672.18	9.97*
2,4,0	5568.41	−3.22	4,4,0	8093.61	1.04	0,9,2	9696.16	1.83*
2,0,2	5701.41	2.79	4,0,2	8120.70	−0.90	3,8,0	9716.70	12.72*
1,6,0	5762.23	−0.65	1,1,4	8174.27	0.97	3,4,2	9731.72	−0.50
1,2,2	5898.94	0.95	0,11,0	8178.27	−3.68	0,5,4	9780.98	−2.99
4,1,0	5930.66	−0.19	0,7,2	8264.28	0.83	3,0,4	9796.80	−15.01*
0,8,0	5965.61	0.38	3,6,0	8284.17	3.74	6,3,0	9855.68	7.63*
0,4,2	6101.80	0.09	3,2,2	8330.35	2.06	0,1,6	9904.99	8.33*
3,3,0	6112.11	−2.59	0,3,4	8382.64	−2.64	2,10,0	9920.43	10.15*
0,0,4	6275.98	−4.04	6,1,0	8441.44	6.69*	2,6,2	9950.41	−2.24
2,5,0	6299.70	−2.34	2,8,0	8482.12	8.52*	5,1,2	9984.14	−6.28
2,1,2	6414.16	3.27	2,4,2	8542.25	0.40			

Note. An asterisk indicates that a level was removed from the fit.

TABLE 4
Observed Odd Symmetry Vibrational Term Values (*8*) and Observed Minus Calculated Values (cm^{-1})

(ν_1,ν_2,ν_3)	Obs	O−C	(ν_1,ν_2,ν_3)	Obs	O−C	(ν_1,ν_2,ν_3)	Obs	O−C
0,0,1	1616.85	−2.78	3,2,1	6872.10	2.76	4,3,1	8797.95	3.21
0,1,1	2355.15	−2.44	0,3,3	6897.37	−1.35	1,4,3	8816.65	0.57
1,0,1	2906.07	−0.69	2,4,1	7072.23	0.92	1,0,5	8941.28	0.63
0,2,1	3092.48	−1.51	2,0,3	7192.23	1.89	0,10,1	8944.50	−1.65
1,1,1	3637.84	−0.56	1,6,1	7277.83	1.13	3,5,1	9008.77	1.48
0,3,1	3829.34	0.16	4,1,1	7386.33	4.74	0,6,3	9029.44	−0.70
2,0,1	4179.94	1.34	1,2,3	7403.04	1.97	3,1,3	9065.47	−1.05
1,2,1	4369.10	0.26	0,8,1	7492.23	1.69	6,0,1	9101.27	−2.80
0,4,1	4564.22	0.87	3,3,1	7587.04	2.43	0,2,5	9148.84	−3.17
0,0,3	4754.21	−4.59	0,4,3	7609.57	−0.46	2,7,1	9220.73	2.62
2,1,1	4905.52	1.86	0,0,5	7766.28	−3.86	2,3,3	9281.74	2.20
1,3,1	5098.00	−0.04	2,5,1	7791.18	1.24	5,2,1	9310.32	−0.81
0,5,1	5298.16	1.54	2,1,3	7888.16	3.76	1,9,1	9436.85	1.23
3,0,1	5437.54	3.11	5,0,1	7903.54	1.17	1,5,3	9500.17	2.42
0,1,3	5469.66	−3.69	1,7,1	8000.93	1.84	4,4,1	9518.26	−3.11
2,2,1	5630.36	2.64	4,2,1	8093.10	3.90	4,0,3	9531.08	−16.26*
1,4,1	5826.29	0.41	1,3,3	8110.13	1.09	1,1,5	9623.58	−1.66
1,0,3	5984.71	1.06	0,9,1	8218.84	−0.43	0,11,1	9654.17	−16.46*
0,6,1	6030.71	1.73	3,4,1	8299.45	1.96	3,6,1	9713.52	0.23
3,1,1	6156.25	3.87	0,5,3	8320.00	−0.55	0,7,3	9736.30	−2.30
0,2,3	6183.61	−2.94	3,0,3	8374.58	−3.83	3,2,3	9753.30	−2.49
2,3,1	6351.40	0.99	0,1,5	8457.15	−4.53	6,1,1	9797.03	−4.99
1,5,1	6552.84	0.66	2,6,1	8507.33	1.57	0,3,5	9836.38	−5.00
4,0,1	6676.86	4.29	2,2,3	8585.54	3.44	2,8,1	9928.47	2.35
1,1,3	6693.12	0.52	5,1,1	8608.92	1.31	2,4,3	9976.50	0.86
0,7,1	6761.44	1.09	1,8,1	8721.11	2.18			

Note. An asterisk indicates that a level was removed from the fit.

purposes of comparison. The agreement of these levels with experiment was good. The error in observed minus calculated energies was found to vary from 0.008 cm^{-1} to around 2 cm^{-1}; see Table 5. This is significantly better than that found by VJ for their potential (*31*). Of course, NO_2 is a considerably heavier system than water. This means that low N rotational energies are sensitive mainly to the equilibrium geometry.

Finally, Fig. 1 compares a cut through our potential with previous spectroscopically determined ground state potentials. Besides the obvious point that our potential has removed the unphysical minima in this cut, it is interesting to note that the shape of potential is also somewhat different from Xie and Yan's.

IV. CONCLUSIONS

Tests on previous spectroscopically determined potentials have shown that some of these have problems. In particular, a seemingly excellent water potential was found to give unacceptably poor results for rotationally excited states, while several ground state NO_2 potentials were found to contain unphysical minima (holes).

We have significantly improved the spectroscopically

TABLE 5

Rotational Term Values (*13*) (cm^{-1}) and Observed Minus Calculated Using Our Potential

Level 0,0,0			Level 0,1,0			Level 1,0,0			Level 0,2,0			Level 0,0,1		
	Obs	O−C		Obs	O−C		Obs	O−C		Obs	O−C		Obs	O−C
0_{00}	0.0	0.0	0_{00}	749.65	−0.24	0_{00}	1319.79	−1.84	0_{00}	1498.34	−1.84	0_{00}	1616.85	−1.84
1_{11}	8.41	−0.11	1_{11}	8.78	−0.01	1_{11}	8.50	−0.13	1_{11}	9.18	−0.13	1_{01}	0.84	−0.13
2_{02}	2.53	−0.03	2_{02}	2.53	−0.03	2_{02}	2.52	−0.02	2_{02}	2.53	−0.02	1_{10}	8.20	−0.13
2_{11}	10.15	−0.06	2_{11}	10.52	0.06	2_{11}	10.92	0.62	2_{11}	10.92	0.62	2_{12}	9.83	−0.02
2_{20}	32.81	−0.42	2_{20}	34.29	0.04	2_{20}	33.17	−0.52	2_{20}	35.89	−0.52	2_{21}	31.90	0.62
3_{13}	12.57	−0.15	3_{13}	12.94	−0.04	3_{13}	12.64	−0.17	3_{13}	13.33	−0.17	3_{03}	5.03	−0.52
3_{22}	35.34	−0.45	3_{22}	36.81	0.01	3_{22}	35.69	−0.55	3_{22}	38.42	−0.55	3_{12}	12.45	−0.17
3_{31}	73.07	−0.94	3_{31}	76.36	0.09	3_{31}	73.88	−1.16	3_{31}	79.94	−1.16	3_{21}	34.41	−0.55
4_{04}	8.44	−0.09	4_{04}	8.43	−0.10	4_{04}	8.39	−0.08	4_{04}	8.42	−0.08	3_{30}	71.02	−1.16
4_{13}	16.14	0.04	4_{13}	16.50	0.16	4_{13}	16.18	0.03	4_{13}	16.90	0.03	4_{23}	37.77	−0.08
4_{22}	38.72	−0.49	4_{22}	40.19	−0.03	4_{22}	39.05	−0.58	4_{22}	41.79	−0.58	4_{32}	74.38	0.03
4_{31}	76.45	−0.98	4_{31}	79.74	0.05	4_{31}	77.24	−1.20	4_{31}	83.31	−1.20	4_{41}	125.43	−0.58
4_{40}	129.06	−1.67	4_{40}	134.82	0.15	4_{40}	130.47	−2.06	5_{24}	46.00	−0.62	5_{05}	12.58	−1.20
5_{15}	20.07	−0.24	5_{15}	20.42	−0.13	5_{15}	20.08	−0.24	5_{33}	87.52	−1.24	5_{14}	41.96	−2.06
5_{24}	42.94	−0.54	5_{24}	44.41	−0.09	5_{24}	43.24	−0.62	5_{51}	219.08	−2.10	5_{23}	78.58	−0.24
5_{33}	80.68	−1.02	5_{33}	83.95	−0.00	5_{33}	81.43	−1.24				5_{32}	129.63	−0.62
5_{42}	133.23	−1.76	5_{42}	139.04	0.09	5_{42}	134.67	−2.10				5_{41}	194.92	−2.10
5_{51}	200.55	−2.59	5_{51}	209.41	0.20									

determined potential for the electronic ground state of NO_2 constructed by Tashkun and Jensen (*13*). This improvement has been achieved by use of a Hamiltonian based on the use of an exact kinetic energy operator and by taking care to eliminate artificial holes from physical regions of the potential.

Unlike most previous spectroscopic determinations of NO_2 potentials (*14, 15, 20*) and Xie and Yan's recent water potential (*6*), we have tested our new potential against rotational term values for NO_2. We regard this step as vital for proving that the potential obtained is indeed physical.

Finally, one must remember that NO_2 is actually a classic case of Born–Oppenheimer failure. In this work we have performed our fits to a single potential function, representing the electronic ground state of the system. However, nonadiabatic calculations on this system by Hirsch, Buenker, and Petrongolo (*18–20*) strongly suggest that many vibrational states lying 5000 cm^{-1} or more above the vibrational ground state are perturbed by interactions with the low-lying $\tilde{A}^2B_2$ state. As the majority of the vibrational levels used in this work lie in this perturbed region, the resulting potential energy surface must be regarded as an effective one which in some part includes contributions from these nonadiabatic interactions.

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