Infrared Spectra of N 2O–Hydrogen Complexes

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Infrared spectra of N$_2$O–hydrogen complexes

Jian Tang and A. R. W. McKellar
*Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa,
Ontario K1A 0R6, Canada*

The infrared spectra of five distinct species of N$_2$O–hydrogen van der Waals complexes
(N$_2$O–paraH$_2$, –orthoH$_2$, –orthoD$_2$, –paraD$_2$, and –HD) were studied in the region of the ν_1
fundamental band of N$_2$O ($\approx$2224 cm^{-1}) by tunable diode laser spectroscopy in a pulsed supersonic
jet expansion. The spectra corresponded to those of T-shaped asymmetric rotors with mainly a-type
transitions ($\Delta K_a = 0$), plus weaker b-type transitions ($\Delta K_a = \pm 1$) in the case of N$_2$O–D$_2$. They
were analyzed using a conventional Hamiltonian with quadratic centrifugal distortion parameters.
The fitted rotational parameters were consistent with structures having intermolecular separations
between 3.25–3.4 Å and angles of about 80° between the N$_2$O axis and the hydrogen
center-of-mass. These intermolecular distances are about 0.3 Å shorter than those observed
previously for the related system, OCS–hydrogen. The band origins were blueshifted relative to the
free N$_2$O molecule by from +0.25 to +0.79 cm^{-1}. These vibrational shifts showed regularities
among the different spin and isotopic forms of hydrogen that were analogous to those in OCS–
hydrogen. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1514207]

I. INTRODUCTION

We recently reported the observation and analysis of in-
frared spectra of isolated OCS–^{4}He and OCS–hydrogen van
der Waals complexes,[1,2] including all the experimentally ac-
cessible nuclear spin and isotopic forms of hydrogen, namely
paraH$_2$, orthoH$_2$, orthoD$_2$, paraD$_2$, and HD. The results
were of special interest because OCS has been a favorite
spectroscopic probe in ultracold helium nanodroplet
experiments,[3–8] and because analogous spectra of the same
OCS–hydrogen complexes have themselves been studied in
He nanodroplets by Grebenev *et al.*[9–11]

In subsequent work,[12] we also examined OCS–^{3}He and
moved to a closely related chromophore, nitrous oxide, to
study N$_2$O–^{3}He and N$_2$O–^{4}He spectra. The present paper
represents a further extension of this research, namely a char-
acterization of N$_2$O–hydrogen complexes by means of high
resolution spectroscopy carried out with a pulsed supersonic
jet expansion and a tunable infrared diode laser probe. As in
the OCS–hydrogen case, we have found that the spectra can
be successfully analyzed in terms of an approximately
T-shaped structure using an ordinary asymmetric rotor
Hamiltonian. The spectra are predominantly a-type in struc-
ture ($\Delta K_a = 0$), with weaker b-type transitions ($\Delta K_a
= \pm 1$) sometimes detected, and there are striking regulari-
ties in the vibrational shifts, rotational parameters, and ap-
proximate derived structures. As well, there is no evidence
for any direct effect of the angular momentum, $j_H = 1$, car-
ried by the orthoH$_2$ and paraD$_2$ species on the ground state
energy levels of their complexes with OCS or N$_2$O.[13]

Carbonyl sulphide and nitrous oxide are members of the
"carbon dioxide molecular family." All three molecules
(OCS, N$_2$O, and CO$_2$) have strong fundamental infrared
transitions in the 2000–2400 cm^{-1} region, which is one rea-
son why these species are useful probes for the nanodroplet

experiments.[14] The infrared spectrum of CO$_2$–^{4}He has been
studied previously,[15] but not the CO$_2$–hydrogen complexes,
as far as we are aware. Microwave pure rotational spectra
have been reported for OCS–^{4}He,[16] CO$_2$–^{4}He,[17] and
OCS–hydrogen,[18] but not for N$_2$O–hydrogen.

II. RESULTS AND ANALYSIS

A. Experimental details

The apparatus has been described previously.[19,20] A tun-
able Pb–salt infrared diode laser is operated in rapid scan
mode[21] and a toroidal mirror system reflects the laser beam
182 times through a pulsed supersonic slit jet expansion. The
spectrum is calibrated by simultaneously recording spectra of
a temperature-stabilized étalon and a standard reference gas
(N$_2$O).[22,23] The expansion gas consisted of a mixture of
about 0.2% N$_2$O plus 20% hydrogen in helium carrier gas,
with a backing pressure of 5 atm. The low temperature equi-
librium species, paraH$_2$ and orthoD$_2$, were prepared in a
conventional batch process and mixed with the other gases as
described previously for the OCS–hydrogen experiment.[2]

B. N$_2$O–orthoH$_2$

Normal hydrogen consists of 25% paraH$_2$ and 75%
orthoH$_2$. At the very low temperatures of our jet expansion
($\approx$2 K), these correspond exclusively to hydrogen molecules
in the $j_H = 0$ and 1 rotational states, respectively. In our first
experiments using a mixture of helium+normal hydrogen
+N$_2$O, we expected to observe, and indeed did observe,
only a single spectrum, that of N$_2$O–orthoH$_2$. This result
was just the same as for OCS–hydrogen,[2] and is presumed to
occur because the N$_2$O–orthoH$_2$ complex is more strongly
bound than N$_2$O–paraH$_2$ (and N$_2$O–He) and therefore
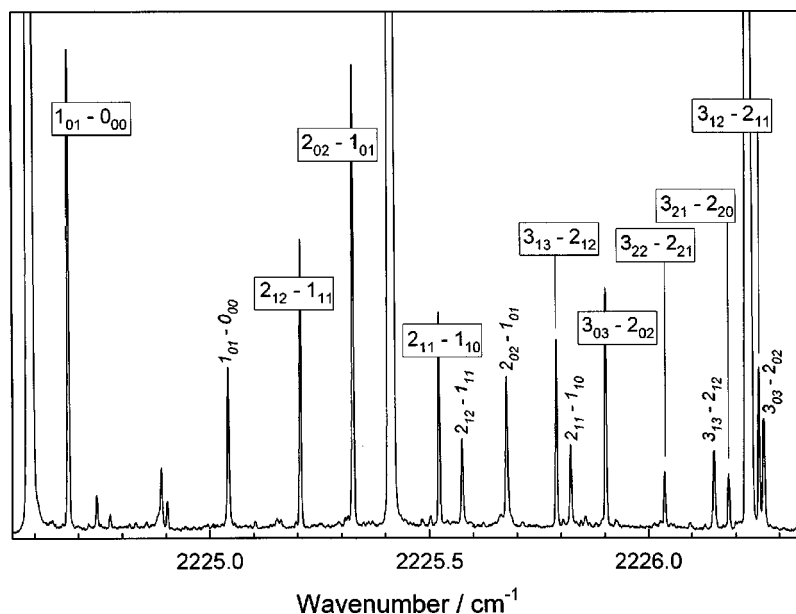comes to completely dominate in the cold dynamic environ-

FIG. 1. A portion of the infrared spectrum of N_2O-H_2 complexes observed using an expansion gas mixture of N_2O, para-enriched H_2, and He. Rotational assignments ($J_{K_aK_c} \leftarrow J_{K_aK_c}$) are shown for N_2O–paraH$_2$ (horizontal text enclosed in rectangles) and for N_2O–orthoH$_2$ (vertical italic text).

ment of the jet expansion. Of course, there are also many uncomplexed N_2O monomers in the expansion, along with N_2O dimers, which are much more strongly bound than N_2O–hydrogen or –helium. However, the concentration of N_2O dimers is minimized by the small fraction ($\approx 0.2\%$) of N_2O in the gas mix, and the spectrum of $(N_2O)_2$ is (very fortunately) shifted about 5.7 cm^{-1} to higher wave numbers, well out of our present region of interest.[24]

The spectrum of N_2O–orthoH$_2$ was quite easy to assign thanks to the similarities with OCS–hydrogen. It consisted of the parallel band ($\Delta K_a = 0$) of a prolate asymmetric rotor molecule, with perpendicular ($\Delta K_a = \pm 1$) transitions being too weak to assign with confidence. Part of the problem in locating $\Delta K_a = \pm 1$ transitions was the presence of a background of unidentified weaker lines in the spectrum. These unidentified lines could be due to an impurity species (e.g., N_2O–H_2O) or to transitions of N_2O–orthoH$_2$ in an excited vibrational state; the problem is discussed further below. A total of 44 transitions of N_2O–orthoH$_2$ were assigned, with K_a-values ranging from 0 to 2, and J-values from 0 to 6. The measured line positions and assignments are listed in a supplementary table available through EPAPS.[25] A few lines involving $K_a = 3$ levels were also observed at their expected positions, but they were too weak and/or overlapped to measure accurately.

C. N₂O–paraH₂

By using a sample of para-enriched hydrogen, we were easily able to observe a distinct spectrum for N_2O–paraH$_2$. But even though the para concentration was well over 95% (there was no direct way to measure the enrichment), the spectrum of N_2O–orthoH$_2$ persisted with an intensity about one-third that of N_2O–paraH$_2$, as illustrated by the spectrum of Fig. 1. This effect is similar to that encountered[2] with OCS–H$_2$, and is due to the stronger binding energy of the ortho complex. In the present case, we were able to achieve a relatively stronger paraH$_2$ spectrum, due either to better enrichment or to less binding energy effect.

We assigned 53 transitions to the N_2O–paraH$_2$ complex, with $K_a = 0$ to 3, and $J = 0-6$, and these are listed in the supplementary tables.[25] But even though the spectrum was somewhat cleaner than that of N_2O–orthoH$_2$, we were still unable to confidently assign any $\Delta K_a = \pm 1$ transitions. It may be noted in Fig. 1 that the N_2O–paraH$_2$ spectrum is significantly shifted (-0.4 cm^{-1}) to lower wave numbers, compared to the N_2O–orthoH$_2$ spectrum. A similar, but smaller (-0.1 cm^{-1}) shift was observed for the analogous OCS complexes.[2]

D. N₂O–paraD₂ and N₂O–orthoD₂

Normal deuterium gas is composed of 33% paraD$_2$, with $j_H = 1$, and 67% orthoD$_2$, with $j_H = 0$. As in the H$_2$ case, we observed the spectrum of the more strongly bound $j_H = 1$ species by using normal D$_2$ in our gas mix, and then detected the $j_H = 0$ species by using an enriched orthoD$_2$ sample. In this case, the enrichment achieved was clearly inferior, because the observed relative strength of the $j_H = 0$ to $j_H = 1$ transitions was only about one-third, but this still sufficed to adequately measure the N_2O–orthoD$_2$ spectrum.

We assigned 82 transitions to N_2O–paraD$_2$, with $K_a = 0$ to 4, and $J = 0-7$, as listed in the supplementary tables.[25] Some weak transitions involving $K_a = 5$ levels were detected close to their expected positions, but these were not included in the analysis. The N_2O–orthoD$_2$ results were somewhat less extensive, with 50 transitions having $K_a = 0-3$, and $J = 0-7$. For both spin species, the assignments included a number of b-type $\Delta K_a = \pm 1$ transitions, and even some a-type transitions with $\Delta K_a = \pm 2$, which can have significant intensity since N_2O–D$_2$ is fairly close to the oblate limit, as discussed below.

E. N₂O–HD

At the low temperatures of the jet expansion, HD molecules will all relax to their lowest rotational state, $j_H = 0$, since there are no symmetry restrictions. Therefore the

TABLE I. Molecular parameters for N_2O–hydrogen complexes (in cm^{-1}).

	N_2O–pH_2 $j_H=0$	N_2O–oH_2 $j_H=1$	N_2O–pD_2 $j_H=0$	N_2O–pD_2 $j_H=1$	N_2O–HD $j_H=0$
			Ground state		
A	$0.80057(31)^a$	$0.83416(106)$	$0.460364(59)$	$0.464186(40)$	$0.56677(22)$
B	$0.431023(38)$	$0.397233(81)$	$0.413182(36)$	$0.395766(22)$	$0.427465(50)$
C	$0.268863(30)$	$0.270198(74)$	$0.211735(22)$	$0.213182(12)$	$0.235160(30)$
Δ_K	$0.012(109)\times10^{-3}$	$-0.17(56)\times10^{-3}$	$0.301(12)\times10^{-3}$	$0.008(47)\times10^{-4}$	$0.153(51)\times10^{-3}$
Δ_{JK}	$0.6293(40)\times10^{-3}$	$0.3832(40)\times10^{-3}$	$-0.1795(92)\times10^{-3}$	$0.0883(21)\times10^{-3}$	$0.3073(55)\times10^{-3}$
Δ_J	$0.1217(84)\times10^{-4}$	$-0.1404(53)\times10^{-4}$	$0.592(13)\times10^{-4}$	$0.511(46)\times10^{-5}$	$0.157(10)\times10^{-4}$
δ_K	$0.426(14)\times10^{-3}$	$0.099(42)\times10^{-3}$	$-0.0104(46)\times10^{-3}$	$0.400(15)\times10^{-4}$	$0.279(13)\times10^{-3}$
δ_J	$0.054(43)\times10^{-5}$	$-0.0909(61)\times10^{-4}$	$0.2772(64)\times10^{-4}$	$-0.006(23)\times10^{-5}$	$-0.27(63)\times10^{-4}$
			Excited state		
ν_0	$2223.9828(1)$	$2224.3805(1)$	$2224.2101(1)$	$2224.5467(1)$	$2224.0747(1)$
A	$0.79872(30)$	$0.83192(104)$	$0.458634(57)$	$0.462822(45)$	$0.56545(21)$
B	$0.427441(32)$	$0.393621(91)$	$0.410075(32)$	$0.392247(26)$	$0.423761(55)$
C	$0.267110(25)$	$0.268315((78)$	$0.210531(17)$	$0.211867(17)$	$0.233768(32)$
Δ_K	$0.011(108)\times10^{-3}$	$-0.11(56)\times10^{-3}$	$0.316(8)\times10^{-3}$	$-0.110(48)\times10^{-4}$	0.153×10^{-3b}
Δ_{JK}	$0.6246(30)\times10^{-3}$	$0.3851(44)\times10^{-3}$	$-0.2002(74)\times10^{-3}$	$0.1004(31)\times10^{-3}$	0.3073×10^{-3b}
Δ_J	$0.1128(68)\times10^{-4}$	$-0.1804(87)\times10^{-4}$	$0.590(12)\times10^{-4}$	$0.100(69)\times10^{-5}$	0.157×10^{-4b}
δ_K	$0.421(12)\times10^{-3}$	$0.096(42)\times10^{-3}$	$-0.0077(37)\times10^{-3}$	$0.415(16)\times10^{-4}$	0.279×10^{-3b}
δ_J	$0.152(38)\times10^{-5}$	$-0.1032(51)\times10^{-4}$	$0.2676(64)\times10^{-4}$	$-0.138(35)\times10^{-5}$	-0.27×10^{-4b}

[a]Uncertainties in parentheses correspond to 1σ from the least squares fit expressed in units of the last quoted digit.

[b]For N_2O–HD, excited state centrifugal distortion parameters were fixed to ground state values (see text).

N_2O–HD spectrum is expected to most closely resemble those of the $j_H=0$ species, N_2O–paraH_2 and N_2O–orthoD_2. The present N_2O–HD experiment was performed using a rather small and old sample of HD. In the resulting spectrum, transitions of both N_2O–orthoH_2 and –paraD_2 were observed with strengths somewhat greater than the desired N_2O–HD transitions, indicating that the isotopic purity of this sample was not very good (but probably still over about 90%, since the more strongly bound $j_H=1$ N_2O–orthoH_2 and –paraD_2 complexes will tend to dominate over the $j_H=0$ N_2O–HD complex in the jet expansion). At any rate, using the fact that the spectroscopic properties of N_2O–HD tended to lie midway between those of N_2O–paraH_2 and N_2O–orthoD_2, it proved relatively straightforward to measure and assign 26 transitions of N_2O–HD. These transitions had values of $K_a=0-3$, and $J=0-5$, and they are listed in the supplementary tables.[25] As in the N_2O–H_2 spectra, all transitions were a-type, with $\Delta K_a=0$.

F. Molecular parameters

We analyzed the spectra using a conventional a-reduced asymmetric rotor Hamiltonian in the type I^r basis.[26] By adjusting the three rotational parameters (A, B, C) and five quadratic centrifugal distortion parameters, very good fits were obtained for all the assigned transitions. The results are listed in Table I. Root mean square residuals ranged from 0.0003 cm^{-1} for N_2O–paraH_2 to 0.0006 cm^{-1} for N_2O–paraD_2. In the case of N_2O–HD, the data were relatively limited (26 transitions), and this fit was therefore made with the ground and excited state centrifugal distortion parameters constrained to be equal. Examination of the other complexes in Table I, where these parameters were fitted independently, shows that this is a good approximation for three out of four cases, including both with $j_H=0$. The exception is

N_2O–paraD_2, where there are significant differences in some distortion parameters between the ground and excited states.

As discussed previously in the case of OCS–hydrogen,[2] it is interesting that a conventional asymmetric rotor analysis works well for these weakly-bound complexes. This is especially true for the $j_H=1$ cases, where we somehow manage to completely ignore the hydrogen angular momentum without any apparent consequences. Part of the explanation for the success of the conventional analysis must be related to the fact that we are only probing the lowest energy quantum states of the complexes, due to the low effective temperature of the jet expansion (≈ 2 K). At some point in the future, when higher energy states are measured, the hydrogen angular momentum must manifest itself and the simple analysis will break down.

III. DISCUSSION

A. Band origins

The observed band origins for the five N_2O–hydrogen complexes studied here are all shifted to the blue relative to the free N_2O molecule (2223.7567 cm^{-1}),[22] by amounts ranging from +0.25 to +0.79 cm^{-1}, as illustrated in Fig. 2. There are obvious regularities in the shifts, with the $j_H=1$ species, N_2O–orthoH_2 and N_2O–paraD_2, having considerably larger shifts than the $j_H=0$ ones, and the shifts increasing in going from H_2 to HD to D_2. It is very interesting to compare this behavior with that observed for the OCS–hydrogen complexes, as shown in Fig. 5 of Ref. 2. The qualitative appearance of the two graphs is almost identical, except that the y-axis for OCS–hydrogen is rather different, involving red (negative) vibrational shifts rather than the blueshifts observed here. This trend, that vibrational shifts in N_2O complexes tend to be more blue than in OCS com-
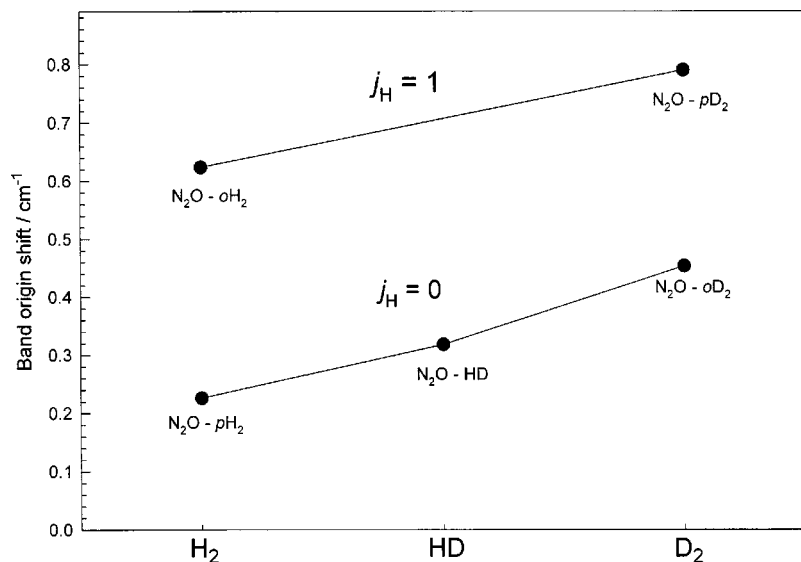
FIG. 2. A plot showing the observed shifts of the band origin for five species of N_2O–hydrogen complexes relative to the free N_2O molecule.

plexes, has already been well documented in the case of rare gas partners,[12,27] but the striking similarities between the OCS–hydrogen and N_2O–hydrogen vibrational shifts show that the observed regularities must be real, and not just accidental.

The vibrational shifts reported recently for N_2O–He complexes ($+0.253$ and $+0.217$ cm^{-1} for the ^{4}He and ^{3}He isotopomers)[12] are very close to that observed here for N_2O–paraH$_2$ ($+0.226$ cm^{-1}). However, this correspondence does not extend to the OCS case, where the He shifts are positive ($+0.1$ cm^{-1}) (Refs. 1 and 12) and the hydrogen shifts all negative (-0.2 cm^{-1} for OCS–paraH$_2$).[2]

B. Rotational parameters and structures

The fact that b-type transitions were observed only for the N_2O–D$_2$ complexes is directly reflected in the considerably larger uncertainties shown in Table I for the A rotational parameters of the N_2O–H$_2$ and –HD species. The B rotational parameters for the five complexes fall in the range 0.39–0.43 cm^{-1}. These values are all very close to the B-value of the isolated N_2O molecule, 0.419 cm^{-1}. This closeness is a reflection of the basically T-shaped structure of the complexes, in which the a inertial axis is approximately aligned with the N_2O linear axis and the b inertial axis passes approximately through the hydrogen molecule center of mass. Therefore the A parameter has a strong dependence on the hydrogen mass, ranging from ≈ 0.8 cm^{-1} for the N_2O–H$_2$ complexes, through 0.57 cm^{-1} for N_2O–HD, to ≈ 0.46 cm^{-1} for the N_2O–D$_2$ complexes. The N_2O–D$_2$ complexes approach the oblate limit (where $A \approx B > C$), but do not come as close as does N_2O–^{4}He, which is almost an "accidental" oblate symmetric top.[12]

Inertial defects, $1/C - 1/B - 1/A$, are listed in Table II for the present systems. These are normally a measure of deviation from planarity, but here they are more likely a result of Coriolis interactions between the rotational levels of the observed ground state and low-lying vibrational states. The inertial defects for the $j_H=0$ complexes are rather large, but not as large as those for N_2O–He, also shown in Table II for

comparison.[12] In contrast, the inertial defects for the $j_H=1$ complexes are much closer to zero, as was also observed for OCS–hydrogen complexes,[2] but this may just be due to an accidental cancellation of interactions.

The large amplitude motions present in weakly bound complexes make it more difficult to obtain structures from spectra, and, indeed, tend to blur the concept of a unique molecular structure. Nevertheless, it is interesting to apply here the simple stick and ball structural model used previously for similar systems.[28] This model uses as input the fitted A and C rotational parameters for the complex, the known B rotational parameter of the N_2O molecule, and the molecular masses. Results are listed in Table II in terms of R, the separation between the N_2O and hydrogen centers of mass, and θ the angle between the N_2O linear axis and the line passing through the hydrogen center of mass. The results reflect T-shaped structures with $\theta=78°$ to $85°$ and R varying from about 3.25 Å for N_2O–D$_2$ to 3.4 Å for N_2O–H$_2$.

Although the precise significance of the structural parameters may be clouded by large amplitude motions, comparisons among different systems using the same model are of interest. Results for N_2O–He complexes,[12] also shown in Table II, demonstrate very similar θ-values, but larger R values for the same reduced masses. Thus the N_2O–He complexes are less closely bound, by about 0.15 Å, than N_2O–hydrogen complexes. Complexes of N_2O with Ne and

TABLE II. Inertial defects and structural results from a simple "stick and ball" model for N_2O–hydrogen complexes.

	Inertial defect/ μÅ^2	R/Å	θ
N_2O–pH$_2$ ($j_H=0$)	2.53	3.427	80.0°
N_2O–oH$_2$ ($j_H=1$)	−0.26	3.403	77.9°
N_2O–oD$_2$ ($j_H=0$)	2.20	3.277	85.4°
N_2O–pD$_2$ ($j_H=1$)	0.17	3.255	85.4°
N_2O–HD ($j_H=0$)	2.51	3.347	83.2°
N_2O–^{3}He (Ref. 2)	6.2	3.523	80.7°
N_2O–^{4}He (Ref. 2)	4.7	3.393	84.6°

TABLE III. Predicted microwave transitions for N_2O–hydrogen complexes (in MHz).

Rotational transition		Complex				
$J'\ K_a'\ K_c'$	$J''\ K_a''\ K_c''$	N_2O–pH_2	N_2O–oH_2	N_2O–oD_2	N_2O–pD_2	N_2O–HD
1 1 0	1 1 1	4810	3799	6034	5469	5732
2 1 1	2 1 2	14430	11409	18062	16407	17196
1 0 1	0 0 0	20981	20011	18727	18255	19863
2 0 2	1 0 1	40713	39319	32587	32610	36580
2 1 2	1 1 1	37067	36180	31420	31027	33946
2 1 1	1 1 0	46687	43791	43448	41965	45410
1 1 0	1 0 1	15876	16844	7453	7517	9902
2 1 1	2 0 2	21850	21356	18313	16872	18732
1 1 1	0 0 0	32047	33096	20146	20303	24033
2 1 2	1 0 1	48133	49266	32839	33075	38116

Ar show similar angular structures ($\theta \approx 82°$–$84°$), with R values around 3.23 Å for Ne and 3.47 Å for Ar.[29] Comparison with the OCS–hydrogen complexes (Table III of Ref. 2) show that the N_2O complexes are significantly more closely bound (by about 0.3 Å) and more nearly T-shaped ($\approx 80°$ as compared to $\approx 70°$). Interestingly, the $j_H = 0$ complexes have slightly larger R values than their $j_H = 1$ counterparts for N_2O–hydrogen, while the opposite is true for OCS–hydrogen.

of the N_2O–D_2 complexes. Compared to the isovalent OCS–hydrogen complexes, which have been characterized in a similar study,[2] N_2O–hydrogen was more nearly T-shaped in structure and had significantly shorter intermolecular bond lengths. Blueshifts of the N_2O vibrational frequency were observed for N_2O–hydrogen, as compared to redshifts for OCS–hydrogen, but apart from this difference there were striking similarities in the variation of these shifts for the two systems as a function of the various forms of hydrogen.

IV. CONCLUSIONS

The present results may be used to predict the microwave rotational spectra of N_2O–hydrogen complexes. Results are listed in Table III as an aid for future investigations. All the a-type transitions and the b-type transitions for N_2O–D_2 should be reasonably reliable (± 15 MHz), but the b-type transitions for N_2O–H_2 and –HD will be subject to larger errors (and also significantly weaker in strength). Observation of these microwave transitions would improve the precision of the present molecular parameters, particularly the b-type transitions for N_2O–H_2 and –HD.

In some of our observed spectra, there were numerous weaker lines which did not form part of the assigned N_2O–hydrogen systems. Possible explanations for these lines might be: transitions involving excited vibrational states of the N_2O–hydrogen complexes; effects due to unwanted impurities (e.g., N_2O–H_2O complexes); or effects of multimode laser operation. The first alternative (excited state N_2O–hydrogen complexes) would be the most interesting, and such transitions have been reported for CO_2–He by Wieda et al.[15] But so far the origin of our extra lines is not clear.

In conclusion, infrared spectra have been recorded and analyzed for weakly bound N_2O–hydrogen complexes, including all the experimentally accessible forms of molecular hydrogen: paraH_2, orthoH_2, orthoD_2, paraD_2, and HD. The observed spectra demonstrated that the $j_H = 1$ forms (N_2O–orthoH_2 and –paraD_2) are significantly more strongly bound than their $j_H = 0$ counterparts. The spectra were successfully analyzed using a conventional asymmetric rotor Hamiltonian with quadratic centrifugal distortion terms. The observed bands were predominantly a-type ($\Delta K_a = 0$) in structure, but b-type transitions were also detected in the case

[1] J. Tang and A. R. W. McKellar, J. Chem. Phys. **115**, 3053 (2001).
[2] J. Tang and A. R. W. McKellar, J. Chem. Phys. **116**, 646 (2002).
[3] S. Grebenev, J. P. Toennies, and A. F. Vilesov, Science **279**, 2083 (1998).
[4] S. Grebenev, M. Hartmann, M. Havenith, B. Sartakov, J. P. Toennies, and A. F. Vilesov, J. Chem. Phys. **112**, 4485 (2000).
[5] S. Grebenev, M. Havenith, F. Madeja, J. P. Toennies, and A. F. Vilesov, J. Chem. Phys. **113**, 9060 (2000).
[6] M. Kunze, P. R. L. Markwick, N. Pörtner, J. Reuss, and M. Havenith, J. Chem. Phys. **116**, 7473 (2002).
[7] Y. Kwon and K. B. Whaley, J. Chem. Phys. **115**, 10146 (2001).
[8] F. Paesani, F. A. Gianturco, and K. B. Whaley, J. Chem. Phys. **115**, 10225 (2001).
[9] S. Grebenev, B. Sartakov, J. P. Toennies, and A. F. Vilesov, J. Chem. Phys. **114**, 617 (2001).
[10] S. Grebenev, E. Lugovoi, B. Sartakov, J. P. Toennies, and A. F. Vilesov, Faraday Discuss. **118**, 19 (2001).
[11] A. F. Vilesov (private communication, 2001).
[12] J. Tang and A. R. W. McKellar, J. Chem. Phys. **117**, 2586 (2002).
[13] We use j_H for the hydrogen rotational angular momentum, which tends to remain a very good quantum number in weakly bound complexes because of the large energy spacing between hydrogen rotational levels.
[14] The 2224 cm^{-1} vibration of N_2O and the 2062 cm^{-1} vibration of OCS are sometimes labeled ν_3 to emphasize the analogy with the 2349 cm^{-1} vibration of CO_2. But since N_2O and OCS lack a center of symmetry, the correct notation is ν_1.
[15] M. J. Weida, J. M. Sperhac, D. J. Nesbitt, and J. M. Hutson, J. Chem. Phys. **101**, 8351 (1994).
[16] K. Higgins and W. Klemperer, J. Chem. Phys. **110**, 1383 (1999).
[17] Y. Xu and W. Jäger, J. Mol. Struct. **599**, 211 (2001).
[18] Z. Yu, W. Klemperer, and K. Higgins, Paper TD10, 56th Ohio State University International Symposium on Molecular Spectroscopy, Columbus, Ohio, June 11–15, 2001; (private communication).
[19] C. Xia, A. R. W. McKellar, and Y. Xu, J. Chem. Phys. **113**, 525 (2000).
[20] J. A. Anstey, M. D. Brookes, and A. R. W. McKellar, J. Mol. Spectrosc. **194**, 281 (1999).
[21] A. De Piante, E. J. Campbell, and S. J. Buelow, Rev. Sci. Instrum. **60**, 858 (1989).
[22] A. G. Maki and J. S. Wells, NIST Special Publication 821, U.S. Government Printing Office, Washington, D.C., 1991; http://physics.nist.gov/PhysRefData/wavenum/html/contents.html

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[23] G. Guelachvili and K. Narahari Rao, *Handbook of Infrared Standards* (Academic, Orlando, 1986).

[24] H.-B. Qian, W. A. Herrebout, and B. J. Howard, Mol. Phys. **91**, 689 (1997).

[25] See EPAPS Document No. E-JCPSA6-117-020243 for complete tables of the observed line positions for the five complexes studied here, N$_2$O–orthoH$_2$, N$_2$O–paraH$_2$, N$_2$O–paraD$_2$, N$_2$O–orthoD$_2$, and N$_2$O–HD. A direct link to this document may be found in the online article's HTML reference section. The document may also be reached via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.aip.org in the directory /epaps/. See the EPAPS homepage for more information.

[26] J. K. G. Watson, in *Vibrational Spectra and Structure*, edited by J. R. Durig (Elsevier, Amsterdam, 1977), Vol. 6, pp. 1–89.

[27] W. A. Herrebout, H.-B. Qian, H. Yamaguchi, and B. J. Howard, J. Mol. Spectrosc. **189**, 235 (1998).

[28] G. D. Hayman, J. Hodge, B. J. Howard, J. S. Muenter, and T. R. Dyke, J. Mol. Spectrosc. **133**, 423 (1989).

[29] M. S. Ngari and W. Jäger, J. Mol. Spectrosc. **192**, 320 (1998); **192**, 452 (1998).