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Journal of Molecular Structure 599 (2001) 211–217

Journal of
MOLECULAR
STRUCTURE

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Fourier transform microwave spectra of the very weakly bound He–CO_2 dimer[☆]

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Received 24 July 2000; accepted 4 October 2000

Abstract

Spectra of pure rotational transitions of the very weakly bound He–CO_2 van der Waals complex were investigated using a pulsed molecular beam Fourier Transform microwave spectrometer. The complex exhibits very large amplitude internal vibrational motions and the rotational transitions were, as a consequence, difficult to locate and to assign. Eight isotopomers, namely He–CO_2, He–$^{13}CO_2$, He–$OC^{18}O$, He–$O^{13}C^{18}O$, He–$^{18}OC^{18}O$, He–$^{18}O^{13}C^{18}O$, He–$OC^{17}O$, and He–$O^{13}C^{17}O$, were studied in order to establish the assignments. The hyperfine structures due to the quadrupolar ^{17}O nucleus were resolved and analyzed in the two ^{17}O containing isotopomers. The observed nuclear quadrupole hyperfine structures not only provide further confirmation for the assignment but also give new information about the angular anisotropy of the He–CO_2 interaction potential. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: He–CO_2; Rotational spectrum; van der Waals complex; Molecular beam

1. Introduction

He-molecule van der Waals dimers are, in general, characterized by very shallow potential wells (~30 cm^{-1}) and by zero point energy levels that can be located at more than half of the height of the well. These systems exhibit therefore very complex internal dynamics and, as a result, complicated spectroscopic features, making them of interest to both theorists and experimentalists. The small number of electrons in He-molecule systems, relative to the heavier rare gases containing counter parts, makes them attractive systems for high level ab initio calculations. A quantitative knowledge about the interaction between helium atoms and small molecules is also of significant current interest in the context of the exciting high resolution spectroscopic work on dopants embedded in liquid He-clusters [1–4]. In particular, a quantitative understanding of the observed increase of moment of inertia of the dopant molecule inside the He-cluster will require the availability of accurate He-molecule interaction potentials. Spectroscopic investigations of He_n-molecule van der Waals complexes ($n = 1$ to a few) can therefore contribute greatly to this area.

Experimentally, the number of high resolution spectroscopic studies of He-molecule systems is quite limited. This is partially because of the considerable difficulties associated with the synthesis and stabilization of the complexes even in a molecular beam environment, and partially because of the

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[☆] This paper is dedicated to Professor Alfred Bauder in appreciation of his significant contributions to the field of microwave spectroscopy.

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PII: S0022-2860(01)00853-5

complicated spectroscopic patterns which are a consequence of the shallow potential wells [5,6]. For He–CO_2, the only previous high resolution spectroscopic study was reported by Weida et al. [7] who observed the infrared spectra of the complex near the CO_2 asymmetric stretching mode. They found that the complex is a T-shaped asymmetric rotor with very large amplitude vibrational motions, as evidenced by the large positive inertial defect of 8.54 amu Å^2 for the ground state. Furthermore, the first intermolecular bending level, at about 9 cm^{-1} above the ground state, shows spectral patterns that deviate sharply from those expected from an asymmetric rotor model [7]. Theoretically, a number of empirical potentials exist that are based mostly on experiments probing the repulsive parts of the interaction potential energy surfaces[1]. More recently, there have been several reports of ab initio investigations of this dimer [8,9]. It is interesting to note that the barrier connecting the T-shaped and the linear minima on the potential energy surface was predicted to be larger in He–CO_2 than that in Ne–CO_2 in the latest ab initio calculation [9].

In this paper, we report the observation of rotational spectra of He–CO_2 with a pulsed molecular beam cavity Fourier Transform microwave spectrometer. The initial frequency prediction was made using the spectroscopic constants from the earlier infrared paper [7]. Seven new isotopomers, namely He–$^{13}CO_2$, He–^{18}OCO, He–$^{18}O^{13}CO$, He–$^{18}OC^{18}O$, He–$^{18}O^{13}C^{18}O$, He–^{17}OCO, and He–$^{17}O^{13}CO$ were also studied. The nuclear quadrupole hyperfine structures associated with the quadrupolar ^{17}O nucleus (spin $I = 5/2$) in He–$OC^{17}O$ and He–$O^{13}C^{17}O$ were resolved and analyzed to provide valuable new information about the angular wave functions of the complex and thus about the anisotropy of the He–CO_2 interaction potential.

2. Experimental

The spectra were measured with a pulsed molecular beam Fourier Transform microwave spectrometer of the Balle–Flygare type [10], which has been described in detail previously [11]. A microwave power amplifier was used to increase the power of the microwave excitation pulses because of the very small transition dipole moment anticipated. The molecular complexes were generated in a pulsed molecular expansion through a general valve nozzle (series 9, orifice $\varnothing = 0.4$ mm) that is mounted near the center of one of the microwave cavity mirrors [12] such that the molecular expansion travels parallel to the cavity axis. Some modifications were made to the nozzle cap to improve the sensitivity of the spectrometer for Helium containing complexes. The details are described in the isotopic study of the He–OCS complex [13]. The full line width at half height of fully resolved components was ~22 kHz. This is noticeably larger than the line width of 7 kHz obtained with Ne as carrier gas [11], due to faster He expansion and the resulting shorter time of observation. The accuracy of the line positions was estimated to be better than 2 kHz for single unsplit lines.

The gas mixture used for the measurements consisted of 0.1% CO_2 in He carrier gas at a total pressure of ~10 atm. Enriched $^{13}CO_2$ (99% ^{13}C, 5% ^{18}O, Cambridge Isotope Laboratories) was used for the measurements of the He–$^{13}CO_2$ and He–$^{18}O^{13}CO$ isotopomers. Enriched ^{17}OCO, ^{18}OCO, and $^{18}OC^{18}O$ were synthesized by introducing normal CO_2 into a glass container with enriched $H_2{}^{17}O$ (30% ^{17}O, Cambridge Isotope Laboratories) and $H_2{}^{18}O$ (98% ^{18}O, Cambridge Isotope Laboratories), respectively. Similarly, enriched $^{17}O^{13}CO$, $^{18}O^{13}CO$, and $^{18}O^{13}C^{18}O$ were synthesized by introducing the enriched $^{13}CO_2$ (99% ^{13}C, 5% ^{18}O, Cambridge Isotope Laboratories) into a glass bulb containing enriched $H_2{}^{17}O$ (30% ^{17}O, Cambridge Isotope Laboratories) and $H_2{}^{18}O$ (98% ^{18}O, Cambridge Isotope Laboratories), respectively. The mixtures were left standing for at least a day at room temperature. The synthesized CO_2 isotopomer was introduced into the spectrometer sample system by slowly warming the CO_2/H_2O mixture from liquid nitrogen temperature. This was done to minimize the contamination of the sample system with H_2O.

3. Spectral search, assignment, and discussion

The $J_{K_aK_c} = 1_{01} - 0_{00}$ rotational transition for the normal isotopomer was predicted from the spectroscopic constants of the infrared work [7] to be at

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[1] For a list of references, see Ref. [7].

17671 MHz. An extensive search was carried out in the region and two transitions were located. Both of these have fairly small transition dipole moments, about a quarter of that of the Ne–CO_2 complex (0.0244(13) Debye) [14], estimated by comparing the $\pi/2$ microwave excitation pulse lengths. The relative intensities of these two transitions and their relative frequencies suggested that one might be a candidate for the normal isotopomer and the other one for the ^{13}C isotopomer in its natural abundance. However, the frequency of the candidate for the normal isotopomer was about 70 MHz higher than predicted from the infrared constants. Unfortunately, the next higher J transitions are located in the 35 GHz frequency region, outside the operating range of our Fourier Transform microwave spectrometer. It was therefore critical to confirm the assignment with additional information, such as isotopic data and nuclear quadrupole hyperfine structures.

We anticipated large uncertainties in the frequency predictions for other minor isotopomers of He–CO_2 when using the usual rigid structure model. The unusually large inertial defect of 8.54 amu Å^2, determined in the infrared study [7], emphasizes this concern. However, since there was no other information available for the further isotopic studies, we used the ground state geometric parameters obtained in the infrared investigation as the initial starting point. The rotational constants for the various isotopomers were then empirically adjusted to reproduce the same inertial defect as in the normal isotopomer. This procedure worked reasonably well with He–$O^{13}CO$ isotopomer mainly because the ^{13}C substitution produces very little change in the rotational frequencies since the carbon atom is quite close to the center of mass of the complex. The assignment of the weaker observed transition to He–$O^{13}CO$ was thus confirmed by the frequency position and, additionally, by a drastic increase in intensity when enriched $^{13}CO_2$ was used.

The search for the He–$O^{13}C^{18}O$ isotopomer was originally done using the enriched $^{13}CO_2$ sample (99% ^{13}C, 5% ^{18}O). A frequency region of about 400 MHz was scanned and a transition with the right magnitude of transition dipole moment was located at 17619.0744 MHz. This was much higher in frequency than anticipated. Furthermore, the observed intensity was found to be considerably lower than expected, by comparing the intensity of He–$O^{13}CO$ in natural abundance (~1.1%) and that of He–$O^{13}C^{18}O$ (~5% in the enriched sample).

At this point, the samples of $OC^{18}O$, $OC^{17}O$, $O^{13}C^{18}O$, and $O^{13}C^{17}O$ were prepared using enriched $H_2{}^{18}O$ (99%) and $H_2{}^{17}O$ (35%) with normal CO_2 and $^{13}CO_2$ (99%), respectively, to ensure high observable intensity for all the isotopomers under consideration. The intensity of the candidate transition for He–$O^{13}C^{18}O$ increased dramatically upon using the enriched sample prepared with $H_2{}^{18}O$ and $^{13}CO_2$. An intensity increase was also observed when using the sample prepared with $H_2{}^{17}O$ and $^{13}CO_2$. This finding was a surprise initially and caused some concern about the assignment to He–$O^{13}C^{18}O$. The assignment could only be correct if the $H_2{}^{17}O$ sample contained substantial amounts of $H_2{}^{18}O$. This was verified by carrying out parallel experiments on the known transitions of the various isotopomers of Ne–CO_2 [15]. The tests verified a significant percentage of $H_2{}^{18}O$ in the $H_2{}^{17}O$ sample and support therefore the original assignment. A similar search and confirmation procedure was carried out for the rotational transition of He–$OC^{18}O$. It was located 18.5 MHz above the He–$O^{13}C^{18}O$ line, consistent with the measured frequency difference of 22.6 MHz in the He–OCO/He–$O^{13}CO$ pair.

The searches for transitions of the He–$OC^{17}O$ and the He–$O^{13}C^{17}O$ isotopomers were carried with the hopes to resolve their ^{17}O nuclear quadrupole hyperfine structures. This would not only further secure the assignment but would also provide valuable new information about the angular isotropy of the He–CO_2 interaction potential energy surface. In the studies of various isotopomers of Ar–CO_2 [16,17,18] and Ne–CO_2, [14,19] it was found that the transition frequencies of the ^{17}O containing isotopomers could be interpolated from the ^{16}O and ^{18}O data with an accuracy of better than 100 kHz. This interpolation procedure, however, appeared not to work well for the He–CO_2 system. An initial scan of the region where the $J = 1$–0 transitions of the He–$OC^{17}O$ and He–$O^{13}C^{17}O$ isotopomers were expected, was unsuccessful. A wider frequency scan of about 400 MHz with the He–$OC^{17}O$ sample, produced one set of lines, resembling nuclear hyperfine pattern of a $J = 1$–0 transition for a nucleus with spin 5/2. The corresponding hyperfine pattern was

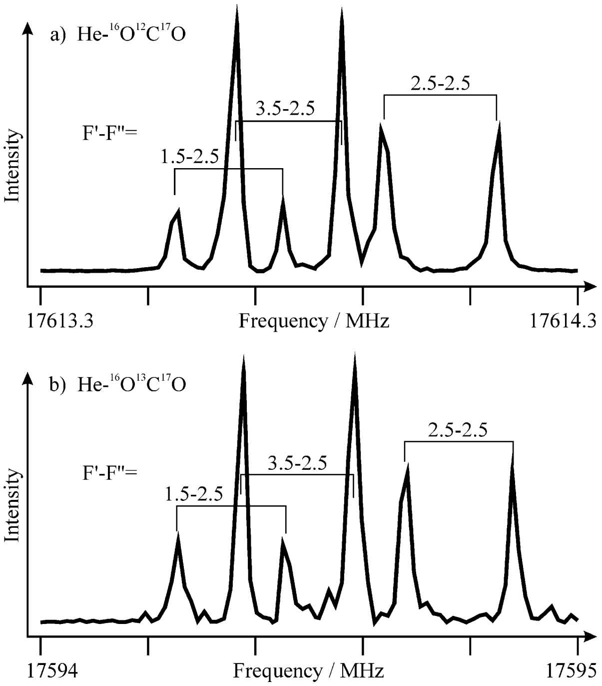

Fig. 1. ^{17}O nuclear quadrupole hyperfine patterns of the $J_{K_aK_c} = 1_{01} - 0_{00}$ rotational transitions of (a) He–OC^{17}O and (b) He–O^{13}C^{17}O. The spectra are composite ones, obtained from a number of experiments at different excitation frequencies. For spectrum (a) four individual experiments were recorded, each with 100 averaging cycles. Six individual experiments with 500 averaging cycles each were used for spectrum (b).

also found for the He–O^{13}C^{17}O isotopomer. The frequency difference between the He–OC^{17}O and He–O^{13}C^{17}O transitions is about 19.3 MHz, consistent with the differences in the He–OCO/He–O^{13}CO and He–OC^{18}O/He–O^{13}C^{18}O pairs. These two sets of hyperfine components are shown in Fig. 1, together with the quantum number assignments. No extra splitting due to spin 1/2 ^{13}C nucleus was detected in case of He–O^{13}C^{17}O. The consistent frequency spacing in the three ^{12}C/^{13}C isotopomer pairs and the observed hyperfine patterns in the ^{17}O containing isotopomers provide a solid foundation for the assignment.

To explain some of the unusual observations mentioned above, such as the poor scaling of the transition frequencies with reduced mass and some inconsistencies in the line intensities, we take a closer look at some interesting differences between the He–CO$_2$ complex and the heavier rare gas–CO$_2$ complexes. For example, substitution of one ^{16}O by ^{18}O in He–CO$_2$ tilts the angle between the C–He intermolecular axis and the a-axis from 0 to 23.7°, while in the case of Ne–CO$_2$ a tilt of only 1.3° results. Substitution of both ^{16}O atoms with ^{18}O switches the a- and b-axes in the case of He–CO$_2$, while the orientation of the principal inertial axis system remains unchanged in Ne–CO$_2$. This helps to explain the low intensity observed for the transition of the He–O^{13}C^{18}O complex. Because of the rotation of the complex in the principal inertial axis system, the a-dipole moment component in He–O^{13}C^{18}O is now only a fraction of the total induced dipole moment between He and CO$_2$. In addition, b-type transitions are now also allowed with the b-component of the dipole moment being of a similar magnitude as the a-component. The larger amplitude vibrational motions in He–CO$_2$, as compared to Ne–CO$_2$, lead also to a smaller average dipole moment. Lastly, the substitution of one ^{16}O with ^{18}O removes the equivalence of the two oxygen atoms, and both $K = 0$ and $K = 1$ levels exist. The $K = 1$ levels can be populated in the beam and effectively reduce the populations in the $K = 0$ levels. In case of substitution of one ^{16}O atom by ^{17}O, the angle tilt is about 7.9° in

Table 1
Relative observed intensities for some He–CO_2 isotopomers

Synthesized	$H_2{}^{18}O$ (98%) + normal CO_2		$H_2{}^{18}O$ (98%) + $^{13}CO_2$ (99% ^{13}C, 5% ^{18}O)		
Frequency/MHz	Rel. Int.	Assignment	Frequency/MHz	Rel. Int.	Assignment
17637.6032	Strong	*a*-type, He–OC^{18}O	17619.0744	Strong	*a*-type, He–O^{13}C^{18}O
17350.0541	Weak	*b*-type, He–^{18}OC^{18}O	17331.8162	Medium	*b*-type, He–^{18}O^{13}C^{18}O
17329.0204	Medium	*b*-type, He–OC^{18}O	17321.9260	Weak	*b*-type, He–O^{13}C^{18}O

He–CO_2, as compared to less than 0.6° in the heavier rare gas–CO_2 complexes.

To support the above argument, we attempted to locate the *b*-type transitions for He–OC^{18}O and He–O^{13}C^{18}O. In a close to 1 GHz scan with 0.15 MHz step size, only two possible candidates with the right magnitudes of the dipole moments were detected for each isotopomer. The sets of two transitions were tentatively assigned to the $J_{K_aK_c} = 1_{11}–0_{00}$ *b*-type transition of He–OC^{18}O and the $J_{K_aK_c} = 1_{11}–0_{00}$ *b*-type transition of He–^{18}OC^{18}O and the corresponding transitions of the ^{13}C substituted isotopomers, respectively. The assignment was based on the consistent spacings between the corresponding transitions of the ^{12}C and ^{13}C isotopomers, sample composition, as will be explained below, and comparison to the initial frequency predictions for these two transitions based on the rigid rotor model.

To confirm that the additional transitions found belong to the doubly substituted He–^{18}OC^{18}O and He–^{18}O^{13}C^{18}O species, the enriched CO_2 samples were again tested with parallel measurements on Ne–CO_2. Transitions of Ne–^{18}OC^{18}O and Ne–^{18}O^{13}C^{18}O were predicted, measured, and identified straightforwardly, thus establishing that the enriched sample contains a significant amount of doubly substituted ^{18}OC^{18}O. It should be noted that the spectra observed using the He/CO_2 sample mixtures are very sparse. In fact, no other low dipole moment transitions than those mentioned above were observed. Careful testing with variation of sample composition verified that these two lines are due to He plus the particular CO_2 isotopomer. The assignment of the transitions to the singly or doubly ^{18}O substituted species is based on their relative intensities (see Table 1). The relative percentage of doubly substituted ^{18}O isotopomer in the ($H_2{}^{18}O$ + $^{13}CO_2$) sample is expected to be higher than that in the ($H_2{}^{18}O$ + CO_2) sample. This is because the enriched $^{13}CO_2$ already contained about 5% ^{18}O. In addition, the $H_2{}^{18}O$/carbon dioxide ratio was higher in the $H_2{}^{18}O$/$^{13}CO_2$ sample than in the $H_2{}^{18}O$/CO_2 sample. This explains the opposite intensity pattern observed for the two *b*-type transitions in the respective ^{12}C and ^{13}C containing isotopomers (see Table 1). Based on all these indicators, there is considerable confidence in

Table 2
Measured transition frequencies (in MHz) of the He–CO_2 isotopomers

	Isotopomer	Frequency	Isotopomer	Frequency
JK_aK_c–JK_aK_c				
101–000	He–^{16}O^{12}C^{16}O	17735.0458	He–^{16}O^{13}C^{16}O	17712.4646
101–000	He–^{16}O^{12}C^{18}O	17637.6032	He–^{16}O^{13}C^{18}O	17619.0744
111–000		17329.0204		17321.9260
111–000	He–^{18}O^{12}C^{18}O	17350.0541	He–^{18}O^{13}C^{18}O	17331.8162
101–000	He–^{16}O^{12}C^{17}O	17613.8194[a]	He–^{16}O^{13}C^{17}O	17594.5391[a]
F–*F*				
2.5–2.5		17614.0340		17594.7636
3.5–2.5		17613.7494		17594.4666
1.5–2.5		17613.6348		17594.3450

[a] The hypothetical unsplit center line frequency.

Table 3
Comparison of the ^{17}O nuclear quadrupole hyperfine constants (in MHz) of He–CO_2 and other rare gas–CO_2 complexes

Complex	He–$^{16}O^{12}C^{17}O$	He–$^{16}O^{13}C^{17}O$	Ne–$OC^{17}O$[a]	Ar–$OC^{17}O$[b]
χ_{aa}	1.342(19)	1.406(14)	1.8311(35)	1.8587(11)
χ_{bb}	–	–	− 4.031(59)	− 3.7661(11)
χ_{cc}	–	–	2.200(59)	1.9074(11)
$\langle\theta_a\rangle$[c] (°)	71.1	72.1	81.5	82.5

[a] Ref. [16].

[b] Ref. [18].

[c] The average angle between the *a*-axis and the axis of the CO_2 monomer, as described in the text.

the assignment of these two sets of *b*-type transitions. The probability that these two sets of transitions, with the expected $^{12}C/^{13}C$ isotopic frequency spacing, belong to some other complex is very low.

No attempt was made to locate the *b*-type transitions of the He–$OC^{17}O$ and He–$O^{13}C^{17}O$ complexes. These transitions were expected to be too weak to be observable because of the lower ^{17}O content in the enriched water sample and the additional hyperfine pattern. Furthermore, the rotation of the principal inertial axis system upon substitution is only about 8° as opposed to 24° for the case of ^{18}O substitution. This results in a much smaller contribution of the total induced dipole moment to the *b*-component.

Table 2 summarizes all the observed microwave transition frequencies and their assignments, including the components of the ^{17}O nuclear quadrupole hyperfine structures. The nuclear quadrupole hyperfine coupling constants were obtained by analyzing the observed hyperfine structure using a first order program. The resulting ^{17}O nuclear quadrupole coupling constants are listed in Table 3, together with the corresponding constants for the heavier rare gas–CO_2 complexes. The values of χ_{aa} obtained from the fits are very similar for the He–$OC^{17}O$ and He–$O^{13}C^{17}O$ isotopomers, further confirming the assignment.

From the coupling constant χ_{aa} and the known monomer coupling constant $\chi_0 = -3.92(9)$ MHz, [20] one can derive an average angle $\langle\theta_a\rangle$ using the expression: $\chi_{aa} = \chi_0\langle P_2(\cos\theta_a)\rangle$. Here, θ_a is the angle between the CO_2 axis and the instantaneous *a*-inertial axis of the complex, P_2 is the second order Legendre polynomial, and the brackets indicate averaging over the ground state vibrational motions. From the value of $\langle\theta_a\rangle$, one can derive the average angle between the He–C bond and the *a*-axis: $(90° - \langle\theta_a\rangle)$. From the values of $\langle\theta_a\rangle$ given in Table 3, angles of 18.9 and 17.9° are obtained for the average angle between the *a*-axis and the He–C bond. In case of a complex with C_{2v} symmetry, this angle represents an average excursion of the rare gas atom from the equilibrium position. In the heavier rare gas–CO_2 complexes, the substitution of one ^{16}O atom by ^{17}O tilts the angle between the He–C van der Waals bond and the *a*-inertial axis only by about 0.6°. The interpretation of $(90° - \langle\theta_a\rangle)$ as an average excursion from the equilibrium position remains therefore still valid. For He–CO_2, however, the same substitution tilts the angle between He–C bond and *a*-axis by about 7.9°. Therefore, there are contributions to $\langle\theta_a\rangle$ from two parts, both the rotation of the complex in the principal axis system as a result of the substitution, and from averaging over the large amplitude vibrational motions about the new equilibrium position.

An attempt was made to approximately separate the contributions to $(90° - \langle\theta_a\rangle)$ from equilibrium structure and large amplitude motions. A numerical one dimensional simulation was done in which values for $P_2(\cos\theta_a)$ were calculated and averaged over a range of angles ϕ around the equilibrium angle between *b*-axis and CO_2 axis of 7.9°. ϕ corresponds to the instantaneous excursion from equilibrium. The average was weighted with a $\cos^2\phi$ type function to approximate the shape of the ground state vibrational wavefunction and normalized. The extreme values of ϕ, i.e. the turning points, were then adjusted until the experimental value for $P_2(\cos\theta_a)$ was reproduced at $\phi_{max,min} = \pm 45°$. The average value for $P_2(\cos\theta_a)$ was then recalculated with the same $\phi_{max,min}$, but with an equilibrium angle between *b*-axis and CO_2 axis of 0°. The resulting value for $\langle\theta_a\rangle$ came to 74°, corresponding to an average excursion from the equilibrium position of about 16°.

The average excursion of 16° from the equilibrium position in He–OC^{17}O is almost twice that determined for Ne–O^{13}C^{17}O (8.5°), consistent with the expected lower anisotropy of the He-atom containing system. This value is also in line with an angle of 15°, that can be determined from the A-rotational constant from the infrared work and the b_0 rotational constant of the CO_2 monomer [21], using $(\sin\theta_a)^2 = A/b_0$.

4. Concluding remarks

In summary, this paper describes a study of the lowest frequency pure rotational transitions of the very weakly bound He–CO_2 complex. Extensive work on isotopically labeled species was done to confirm the rotational assignments. The $J_{K_aK_c} = 1_{01}$–0_{00} transition of the normal isotopomer was found about 64 MHz higher in frequency than predicted from the infrared data. This is in line with the residual, unusually large, standard deviation of the infrared fit of about 72 MHz, which was possibly due to the inadequacies of the semirigid rotor model employed. It was possible to resolve ^{17}O nuclear quadrupole hyperfine structures in the rotational transitions of the He–OC^{17}O and He–O^{13}C^{17}O complexes. The resulting ^{17}O nuclear quadrupole coupling constants indicate an angular zero point vibrational motion of significant amplitude, about twice that found in Ne–CO_2.

Acknowledgements

This work was supported by the Natural Sciences and Engineering Research Council of Canada. Y.X. thanks the Izaak Walton Killam Trust for a postdoctoral fellowship.

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