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Submillimeter-wave spectroscopy of the $K = 2–1$ subband of the Ne–CO complex

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ABSTRACT

The pure rotational spectrum of the Ne–CO van der Waals complex has been measured in the frequency range of 208–230 GHz by using the Cologne supersonic jet spectrometer for terahertz applications (SuJeSTA). Eleven new transitions were assigned as belonging to two *R*- and two *Q*-branches of the $K = 2–1$ subband detected for the first time in the ground vibrational state of CO ($v_{CO} = 0$). Improved molecular parameters of the Ne–CO complex were obtained which allowed for a sensitive test of the available intermolecular potential energy surfaces of the Ne–CO system.

1. Introduction

Ne–CO is one of the best studied van der Waals complexes containing a rare gas atom (Rg) and the CO molecule. The fundamental interest in such systems is explained by their structural simplicity and low binding energy between Rg and CO leading to large amplitude motions within the complex. Investigating Rg–CO complexes (Rg = He, Ne, Ar, Kr, Xe) from the heavy atom system Xe–CO to the light atom system He–CO one can follow the transition from semi-rigidity to nearly free rotation of the CO molecule within the complex [1]. Ne–CO represents the crucial intermediate case between these two limits which serves as a sensitive testbed of calculated potential energy surfaces (PES).

In the first spectroscopic study Randell et al. [2] analyzed the infrared (IR) spectrum of the Ne–CO complex by combining data from a pulsed supersonic jet probed by a tunable IR laser apparatus with data from a long-path cold cell and a Fourier transform infrared (FTIR) spectrometer. The spectra of ^{20}Ne–CO and ^{22}Ne–CO were recorded in the frequency range of the CO stretching vibration mode between 2130 and 2160 cm^{-1}. The rotational levels with $K = 0$ and 1, and those of the bending state $v_2 = 1$, with $K = 0$, have been assigned (the latter only for the excited state $v_{CO} = 1$). Later pure rotational spectra have been observed applying pulsed beam Fourier transform microwave (FTMW) technique in the range of 6–26 GHz [3]. The *a*-type *R*-branch transitions within $K = 0$ of seven isotopologues of Ne–CO as well as within $K = 1$ of ^{20}Ne–CO were measured. The main isotopologue ^{20}Ne–CO has been studied in more detail in the IR frequency range by using a tunable diode laser source with a long-path low-temperature absorption cell [4]. The location of a number of new energy states of the complex, including those with $K = 2$ and 3 for both $v_{CO} = 0$ and 1, and that with $v_2 = 1$ and $K = 0$ for $v_{CO} = 0$ were determined. This work was followed by millimeter-wave (MMW) measurements of pure rotational *b*-type transitions of the $K = 1–0$ subband using an intracavity jet OROTRON spectrometer in the frequency range of 80–150 GHz [5–7]. These measurements included observation of all three ^{20}Ne, ^{21}Ne, and ^{22}Ne isotopic modifications of the complex.

The performed spectroscopic studies provided most accurate data which have been used for testing of a number of PES of Ne–CO [8–12]. A recent semi-empirical exchange-Coulomb model PES [12] gave significantly better agreement with the observed spectra from Refs. [2–7] as well as with bulk mixture properties and beam scattering data [13] as compared to earlier full *ab initio* surfaces [8–10]. A new high quality three-dimensional PES based on coupled cluster CCSD(T) method also showed good agreement with the IR experimental spectra [11].

In the present paper we extend earlier spectroscopic measurements of ^{20}Ne–CO by reporting the first direct observation of the $K = 2–1$ subband in the $v_{CO} = 0$ state. Lines belonging to *R*- and *Q*-branches between the $K = 1$ and 2 stacks were recorded and analyzed.

2. Experimental details

The supersonic jet spectrometer for terahertz applications (SuJeSTA) [14] has been used to record spectra of Ne–CO in the frequency range from 208 to 230 GHz.

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The 13–14.4 GHz output frequency of a synthesizer (Agilent 83650 B) is multiplied by a commercial multiplier chain (Virginia Diodes, Inc.) to obtain output frequencies at 208–230 GHz. The sub-millimeter wave beam intersects a pulsed supersonic jet approximately 5 cm downstream in a perpendicular configuration. A multi-pass optics with 10 paths is used to enhance the signal-to-noise ratio. The absorption signal is detected by a low-noise liquid-He cooled InSb hot electron bolometer of high sensitivity. The frequency of the synthesizer is modulated at 40 kHz and phase sensitive detection of the signal is achieved by a lock-in amplifier in 2*f*-mode operation. In addition to the frequency modulation of the radiation source, an on–off modulation of the jet is used for background subtraction through a pair of boxcar integrators. Data acquisition is taken within a 1 ms time window. The combination of frequency and source modulation (double modulation technique) substantially improves the signal-to-noise ratio and at the same time suppresses standing wave etalon effects.

A gas mixture of 2% of CO in Ne at a backing pressure of 5 bar was used for production of the Ne–CO complex. The gas mixture adiabatically expanded into the multi-pass cell through a 1 mm diameter pulsed pin-hole nozzle at a repetition rate of 30 Hz. The measurements accuracy was estimated to be about 100 kHz.

3. Results and analysis

Previous studies have shown that Ne–CO has an approximately T-shaped structure with an effective intermolecular separation of about 3.65 Å. For this configuration, the CO dipole moment lies along the *b*-inertial axis, and thus the strongest rotational transitions have *b*-type (perpendicular) selection rules, with $\Delta K = 1$.

The following quantum numbers of a conventional semi-rigid molecule basis are used here: υ_{CO} for the CO stretching vibration, υ_2 for the complex bending vibration, *J* for the total angular momentum, *K* for the projection of *J* on the intermolecular axis. Parity labels *e* (+1) and *f* (−1) are used to assign the parity *p* of individual levels according to $p(-1)^J$ symmetry. The stacks of low energy levels with *K* = 0, 1 and 2 in the $\upsilon_{CO} = 0$ state of Ne–CO are shown in Fig. 1 and measured transitions are indicated by arrows.

The rotation of CO within Ne–CO is only slightly hindered and thus an alternative way of assigning energy levels of the complex is that of a free rotor basis set with *j* for the angular momentum of the CO unit, *l* for the end-over-end rotation of the complex and *J* for the total angular momentum. The corresponding notation for energy levels shown in Fig. 1 can be interchanged in the following way: $(J,j,l)_{K=0e} = (J,0,J)$; $(J,j,l)_{K=1e} = (J,1,J-1)$; $(J,j,l)_{K=1f} = (J,1,J)$; $(J,j,l)_{K=2e} = (J,2,J-2)$; $(J,j,l)_{K=2f} = (J,2,J-1)$; $(J,j,l)_{K=0e,v2=1} = (J,1,J+1)$.

The rotational transitions of the *K* = 2–1 subband were predicted using the set of molecular constants from the IR study by McKellar and Chan [4]. The largest difference between measured and predicted frequencies was 36 MHz. As an example Fig. 2 shows the *R*(1) transition of the *K* = 2*e*–1*e* subband recorded in second derivative due to 2*f*-mode detection technique. In total, 11 new transitions were measured and assigned, *R*(1) and *R*(2) of both the *K* = 2*e*–1*e* and the *K* = 2*f*–1*f* subband, *Q*(2),*Q*(3),...,*Q*(7) except *Q*(5) of the *K* = 2*f*–1*e* subband and *Q*(2), *Q*(3) of the *K* = 2*e*–1*f* subband. Higher-*J* *R*-branch lines and higher-*J* *Q*-branch of *K* = 2*e*–1*f* lines lie outside the currently accessible frequency range of the spectrometer. *Q*(5) of *K* = 2*f*–1*e* has not been measured because of a too low output power of the radiation source at this frequency. *Q*(8) of *K* = 2*f*–1*e* was not detected despite an extensive search most probably due to the low population of the *K* = 1*e*, *J* = 8 level caused by the low rotational temperature in the beam.

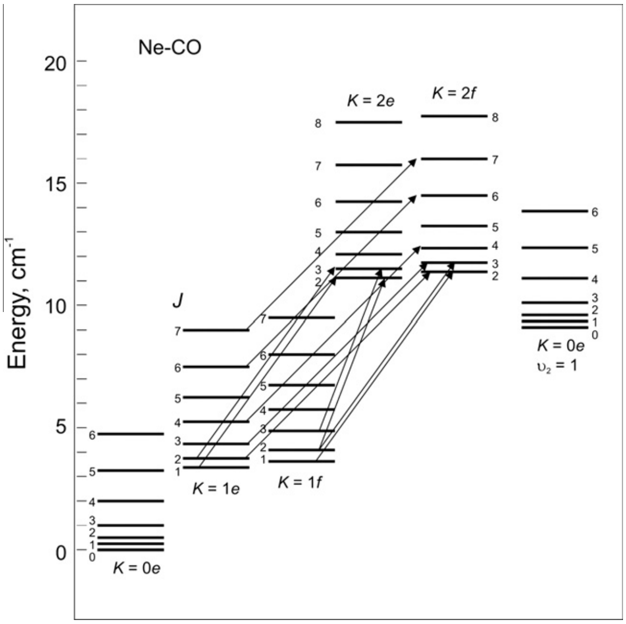

Fig. 1. Low energy level scheme of the Ne–CO complex and measured transitions.

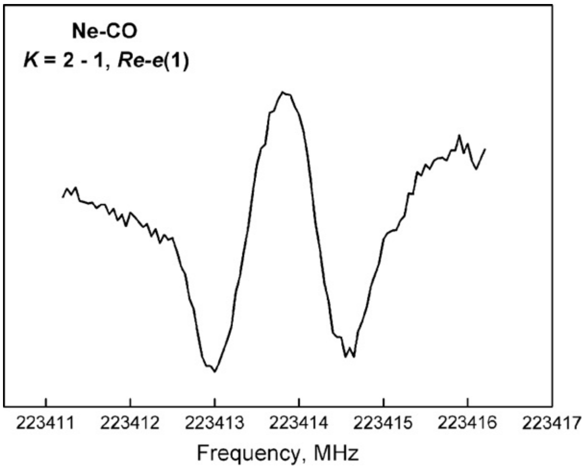

Fig. 2. Line recording of the *R*(1) *K* = 2*e*–1*e* transition of Ne–CO.

The simulated stick spectrum of the *K* = 2–1 subband of Ne–CO is presented in Fig. 3. The frequencies of the newly measured submillimeter-wave transitions are given in Table 1. Line positions were fitted together with available millimeter-wave [5–7] and microwave data [3] using the PGOPHER program, which is open to the public [15]. McKellar and Chan [4] concluded that due to very large asymmetry splitting terms for *K* = 2 and 3 it was preferable in case of Ne–CO to represent each individual stack of levels by a band origin σ plus an independent power series in $J(J+1)$ in contrast to the more common way to represent the asymmetry splitting for the $K \geqslant 1$ states by additional power series. The resulting energy expression for each *K*-stack therefore was extremely simple:

$$E = \sigma + B[J(J+1)] - D[J(J+1)]^2 + H[J(J+1)]^3 + L[J(J+1)]^4,$$

where *B*, *D*, *H*, *L* is a set of rotational parameters. In the fitting procedure the frequencies of the submillimeter-wave, millimeter-wave and microwave transitions were given with relative statistical weights of 1, 2 and 100 according to the corresponding measurement accuracies. Due to the limited number of observed transitions into the *K* = 2*e* stack only the parameters *B* and *D* were fitted