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Spectroscopy of the CO-H_2 van der Waals molecule

May C. Salazar, José L. *Paz* and *Antonio J. Hernández*[*]
Departamento de Química, Universidad Simón Bolívar, Apdo. 89000, Caracas, Venezuela

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Abstract

In the present contribution, we have reviewed the spectroscopic techniques generally used to collect intermolecular interaction data on van der Waals molecules, with special emphasis on the experimental and theoretical background of the spectroscopy of CO-H_2. This analysis showed that the potential energy surface of CO-H_2 had to be recalculated by using a free-parameter fully *ab initio* calculations with basis sets of proven quality. Our fully *ab initio* calculations within the supermolecule approach for the potential energy surface of the diatomic van der Waals CO-H_2 showed that the linear O-C···H-H structure corresponds to the most stable conformation in the ground $CO(X^1\Sigma^+)$-$H_2(X^1\Sigma_g)$ electronic configuration. The calculated dissociation energy corresponded to a D_o of 4.9meV with at least one vibrational state supported by this linear configuration, which agrees well with existing spectroscopic results.

Key words: CO-H_2; spectroscopy; supermolecule; van der Waals molecules.

Espectroscopía de la molécula de van der Waals de CO-H_2

Resumen

En la presente contribución, se han revisado las técnicas espectroscópicas generalmente utilizadas para recolectar datos de interacción intermolecular en las moléculas de van der Waals, con énfasis especial en los antecedentes teóricos y experimentales de la espectroscopía de CO-H_2. Este análisis demuestra que la superficie de energía potencial de interacción de CO-H_2 debe ser recalculada mediante un método completamente *ab initio*, libre de parámetros ajustables y usando funciones de base de reconocida calidad. Nuestros cálculos dentro de la aproximación de supermolécula para la energía potencial del dímero CO-H_2 muestra que la estructura lineal O-C···H-H corresponde al confórmero más estable en *el* estado el&nico fundamental $CO(X^1\Sigma^+)$-$H_2(X^1\Sigma_g)$. La energía de disociación calculada corresponde a D_o = 4,9 meV, con al menos un estado vibracional enlazado en esta configuración, lo cual concuerda con los resultados espectroscópicos existentes.

Palabras claves: CO-H_2; espectroscopía; moléculas de van der Waals; supermolécula.

Introduction

The study of weak molecular interactions has always been a very active research field. Nevertheless, in the last decade there has been a tremendous increase of interest, both by experimentalists and theoreticians, in van der Waals (vdW) molecular clusters.

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[*] To whom correspondence will be addressed.

Molecular clusters are accessible both, to detailed experimental and to reliable quantum mechanical studies. The development of laser techniques for state selective chemistry and spectroscopy and of highly sophisticated molecular beam techniques have contributed to the experimental progress (1-4). The availability of powerful supercomputers and the development of efficient computational algorithms has made possible the quantum mechanical study of the properties of large molecular systems. In spite of the enormous experimental progress in recent years, there have been relatively few experimental studies aimed at investigating the electronic excitation spectra of the simplest diatomic vdW molecules.

Recent developments in non-linear optics have provided tunable and coherent vacuum ultraviolet radiation to obtain high resolution fluorescence electronic excitation spectra. This technique, combined with supersonic beam expansion techniques to form cold vdW molecules, has shown to be a powerful tool for studying interatomic potentials of electronically excited rare gas vdW dimers. But the application of these combined techniques for studying the intermolecular interaction between non- or weakly-polar diatomic-diatomic vdW molecules has not yet been reported. In spite of the relative simplicity of diatomic-diatomic vdW molecules, relatively few excited-state studies have been reported so far, including studies of some of the excited states of CO-H_2 and N_2-H_2 (5).

In the present contribution we review experimental techniques and the experimental and theoretical background on the spectroscopy of CO-H_2. We are also able to describe the interaction energy surface of this vdW molecule in its ground electronic state using standard fully *ab initio* methods of quantum chemistry. Despite many technical difficulties, the *ab initio* methods offer a sound basis for the calculation of vdW potential energy surfaces valid over the whole range of molecular distances and orientations.

Experimental Techniques

Experimental studies of vdW molecules, which constitute the best source of information available to date, can be classified in two big groups according to the way samples are prepared, i.e: (i) Molecular beam, or (ii) Thermal equilibrium studies. Of the several spectroscopic techniques used to study the rotational, vibrational, and electronic spectra of vdW molecule, some of them can be applied to study those complexes which are formed in molecular beams or in thermal equilibrium, while others are only possible to use when only one of these two conditions is fulfilled.

In the molecular beam technique, the gas of interest is expanded through a small hole from a high pressure into a vacuum, in the region immediately down stream of the nozzle, a large number of collisions occur, during which the gas becomes very strongly cooled. Some of the molecules in the expansion will condense to form clusters. By mixing the gas of interest with some inert carrier gas such as Helium or Argon, and by varying the pressure and in some cases by varying the temperature of the nozzle, it is possible to change the size distribution of clusters that are formed in the expansion.

In thermal equilibrium techniques, the gas of interest is contained in an absorption cell under certain temperature and pressure conditions. Here, there exist dimer, trimer, and larger molecular cluster, and the relative concentration of these species is changed by strong cooling.

The procedure used to obtain experimental information on the intermolecular interaction involves two steps: (i) A particular form of this potential is assumed, where some simple well-tested model potentials are commonly used. (ii) The empirical parameters of the model potential are then adjusted until satisfactory agreement is obtained between the calculated and experimental property of interest.

The most common methods used to determine the empirical intermolecular interaction and the geometric and thermodynamic properties of vdW molecules are: (i) Elastic scattering of molecular beams, (ii) Spectroscopic methods as, rotation-vibration and electronic spectroscopy, electron spectroscopy, and nuclear magnetic and electron spin resonance spectroscopy. (iii) Macroscopic properties and transport phenomena.

Methods belonging to group (iii) (e.g., the virial, viscosity and diffusion coefficients and thermal conductivity) were among the most widely used in the past. However, their importance has recently decreased and interest has shifted largely to the first and second group of methods. In particular, determination of intermolecular interaction potentials can be best achieved using spectroscopic techniques involving lasers and molecular beams.

2a. Spectroscopic Methods

Eight different types of spectroscopy for vdW molecules can be distinguished: (i) Absorption spectroscopy, (ii) Molecular beam electric resonance spectroscopy, (iii) Fourier transform molecular beam spectroscopy, (iv) Laser induced fluorescence spectroscopy, (v) Difference frequency spectroscopy, (vi) Matrix isolation spectroscopy, (vii) Electron spectroscopy, and (viii) Nuclear magnetic and spin resonance spectroscopy. The first six techniques measure the spectroscopy constants, which in turn, yield information on the geometry of the vdW molecules under study. The last one is most important for the experimental study of the interaction of molecules in solution or solid matrices.

(2a-i) Absorption Spectroscopy in Long Path Cell (LPGCAS): The method of using a long path in a gas cell represents the oldest of all in the study of van der Waals molecules (6). Here, the gas of interest is contained in an absorption cell under pressure and temperature that may varied. In the gas at equilibrium, dimers, trimers and larger clusters can be present, and the relative concentration of these species may be increased by strong cooling. In this method, the absorption spectrum (measured as the decrease of laser intensity as a function of the laser frequency) is recorded through a long optical path used to increased the concentration of the vdW species present in the cell. An important problem associated to gas cell spectroscopy is that it is difficult to distinguish between different sized clusters. Fortunately, under most circumstances the number of trimers and larger clusters present in the gas is very much less than the number of dimers. Another problem with experiments carried out using a gas cell rather than a molecular beam is the Doppler and pressure broadening of the spectrum, which can be significant and may result in a large reduction in the final resolution that can be attained.

(2a-ii) Molecular Beam Electric Resonance Spectroscopy (MBERS): This method is very effective and yields accurate values for the electric dipole moment and nuclear hyperfine interactions (7), that in turn gives structural information on the vdW molecule under study. In this technique electrostatic state selectors with quadrupolar symmetry act on the molecular dipole moment to focus a molecular beam for certain rotational orientations and defocus the beam for others. Absorption of microwave or radiowave radiation between two such quadrupole state selectors is detected by loss of beam intensity at a mass spectrometer detector when molecules are switched from a focusing to a defocusing level. This technique is very sensitive and yields very high resolution spectra, but requires that the molecule being studied has an appreciable permanent dipole moment. Advantages of this method are the elimination of collision broadening effects and lessening of Doppler broadening. Additionally, it can be used with strong and weak vdW complexes.

(2a-iii) Fourier Transform Molecular Beam Spectroscopy (FTMBS): This represents the most recent of all techniques described here. In this experiments, the molecular beam is directed into a cavity where a several microsecond microwave pulse polarizes systems with a rotational-translational transition corresponding to the bandwidth of the cavity (8). After dissipation of the microwave pulse, the coherent microwave signal is detected by the super heterodyne method and the frequency spectrum is obtained by fourier transformation. The spectral resolution is comparable to MBERS. Both strong and weak intermolecular complexes can be studied.

(2a-iv) Laser-Induced Fluorescence Spectroscopy (LIF): LIF has been broadly used in the study of vdW molecules where one of the components is an atom. A beam of radiation from a tunable laser passes through the gas and the laser frequency connecting a particular transition in the ground electronic state with a vibration-rotation state in the ground or in an excited electronic state. The excited molecule can then fluoresce and the undispersed fluorescence is measured as a function of the excitation frequency (9,10). The molecule must have a strong electronic absorption band in the spectral ranges covered by available lasers. The LIF spectrum is much simpler than the absorption spectrum of the same molecule. The use of LIF allows accurate wavelength measurements to be performed, from which the molecular ground state constant can be determined. The line intensities measured in the fluorescence spectra can also be used to derive Franck-Condon factors. They provide a good test of the vibrational wave functions of the upper and lower states. Although LIF is obviously a very powerful technique, it does have several shortcoming for studying some molecules where the electronic transitions is so weak that it is difficult to excite a substantial fraction of the molecule into the excited electronic state. Even worse is when the emission lifetime is so long that very few of the excited molecules fluoresce while they are in the vicinity of the detection optics. Also, is extremely difficult to rotationally resolve the product states of vibrational predissociation processes using dispersed fluorescence.

(2a-v) Difference Frequency Laser Spectroscopy (DFLS): The difference frequency spectroscopy operates by mixing two laser beams in a nonlinear medium (e.g., a crystal of $LiNbO_3$) the output signal has a frequency which is the difference of the frequency of the inputs beams, normally in the infrared range. This technique has been also used in equilibrium gas cells, and it allows to obtain high-resolution vibrational-rotational spectra in the ground state of vdW molecules (11,12).

(2a-vi) Matrix Isolation Spectroscopy (MIS): In the technique of matrix isolation the atoms or molecule to be studied are mixed with a large excess of an inert gas upon condensation on a cold surface. The inert gas is often Argon in excess by a factor of 1:1000, and the temperature is about 10K (13-15). Although, vibrational spectroscopy of vdW molecules in the solid phase also provides structural information, it must be recalled that matrix molecules interact with the vdW molecule under investigation and that the characteristics of the vdW molecule are affected by many-body interactions.

(2a-vii) Electron Spectroscopy: Photoelectron spectroscopy using ultra violet radiation (PES) provides information on the ionization potentials of vdW molecules. Low pressure working conditions, typical for PES, are used for stable vdW complexes, but supersonic molecular beams techniques are necessary to study weak vdW molecules.

(2a-viii) Nuclear Magnetic and Spin Resonance Spectroscopy: Nuclear magnetic resonance spectroscopy (NMR) is one of the most important methods for the experimental study of the interaction of molecules in solution including quite complex molecules of biological interest, while spin resonance spectroscopy (ESR) is mostly associated with the determination of high spin complexes in solid matrix studies. The use of NMR is based on the fact that spin coupling constants depend on the conformation of the vdW molecule. In ESR, the structural information of the vdW complex is obtained from analysis of the tensor g and from the hyperfine splitting tensor and concretely on whether a pitype or sigma-type compex is involved.

2b. Experimental Evidence of $CO-H_2$

The first spectroscopic evidence of $CO-H_2$ is reported by Welsh et al. in 1967 (16) using LPGCAS in the infrared region at 77°K. In this work, spectra of mixtures of N_2-H_2 and $Ar-H_2$ are also collected and reported identical to the $CO-H_2$ spectra. In general, the observed spectra are of very low resolution because of the collisional broadening caused by the high pressure needed to observe signal for this vdW dimer of low dipole moment. More recently, a well resolved spectra of $CO-H_2$ (and N_2-H_2) has been recorded by McKellar (17,18), using LPGCAS combined with Fourier-transform techniques and optical paths as long as 154 meters to obtain spectral resolutions as low as 0.01 cm^{-1}. In this work, the N_2-H_2 and $CO-H_2$ spectra are also reported as very similar, and although many lines could be assigned by assuming a T-shaped structure, its true conformation is still unknown. Indirect evidence of $CO-H_2$ can be found in measurements of vibrational relaxation times (19) and collisional cross-sections of CO by H_2 (20).

Ab-initio theoretical methods

Ab-initio studies of vdW interaction energies have essentially followed two directions. The first regards the interaction between the subsystems as a perturbation, and partitions the energy into terms such as electrostatic, repulsion, polarization, induction, and dispersion. The second approach considers the interacting subsystems as a supermolecule (1-5,21). The intermolecular perturbation approach is far more suitable for calculations of weak interactions because the interaction energy is obtained directly, rather than as the difference between two numbers usually several orders of magnitude larger than the interaction energy itself. Nevertheless, since all the highly effective *ab initio* methods developed for single-molecule calculations are in principle applicable without change and, it also offers an uniform treatment over the entire range of intermolecular separations, the vast majority of calculations of the interaction energy of vdW complexes are carried out at present using the supermolecule approach.

The interaction energy can be obtained in the framework of the supermolecule approach at the SCF and correlation levels of approximation for the total energy

$$E = E^{SCF} + E^{correlation} . \qquad [1]$$

The interaction energy (IE) is defined as:

$$IE(\mathbf{R}) = E(CO \cdots H_2; \mathbf{R}) - E(CO \cdots X; \mathbf{R}) - E(X \cdots H_2; \mathbf{R}), \qquad [2]$$

where $E(CO \cdots X; \mathbf{R})$ and $E(X \cdots H_2; \mathbf{R})$ are used here to indicate that the monomer energies are derived in the total dimer centered basis set. This amounts to applying the counterpoise procedure of Boys and Bernardi (22) to correct for the basis set superposition error (BSSE) at both the SCF and the correlation levels of approximation at each molecular configuration **R**. Despite the long lasting controversy on its credibility, the function counterpoise method of Boys and Bernardi proves to be the correct approach (23).

3a. Early Theoretical Studies on CO-H_2

Early studies on the potential surface of CO-H_2 have been performed by: (i) combining short range interaction, calculated at the SCF level of approximation, with long range interactions represented by parametric dispersion energies (24,25), (ii) calculating free-parameter ab initio interaction potentials, which combine SCF calculations with intermolecular second-order Hartree-Fock dispersion terms (26,27), (iii) using the MMC (molecular mechanics for clusters) method of Dykstra *et al.* (28), which combines electrical interactions, calculated from high-level *ab initio* calculations, with parametric nonelectrical interactions, (iv) using model potentials in the framework of the electron gas model (29,30). The following observations concerning these theoretical studies are relevant: (i) Some of these theoretical studies favor the **O-C···H-H** (24,31), or the **C-O···H-H** (25) colinear structures, while the rest favor the **parallel** (29), or **almost parallel** (28), structure, as the most stable conformation of CO···H_2, (ii) dynamical studies using the potential energy surface of Schinke et al. (24) have given the best overall description of the experimental differential cross sections and differential energy loss spectra (32-34), and it has also successfully described the role of H_2 rotation in the vibrational relaxation of CO (35,36), and the pressure broadening cross section of CO-H_2 (37).

Although a complete assignment of the CO-H_2 spectra can be achieved by iterative fittings using parametric potential surfaces, which would permit successive refinements and assignments in order to determine an improved potential, we believe that parametric potentials may lack of general validity in so far as they may depend either on the functional forms chosen or on the properties used in fitting the parameters, and consequently, we make use in the present study of a free-parameter fully *ab initio* potential as an alternative. We also feel that previous free-parameter *ab initio* calculations (26,27) are seriously hampered by the problem of basis set superposition error due to the use of basis sets of inadequate size, and in consequence, the ab initio potential energy surface of CO-H_2 has to be recalculated.

3b. Recent Calculations on the $CO(X^1\Sigma^+)$-$H_2(X^1\Sigma_g)$ Ground Electronic State

High-level *ab initio* calculation were performed to determine the conformational structure of the CO-H_2 vdW dimer in its ground electronic state (in the framework of the supermolecule approach) at the RHF-SCF and many-body perturbation theory (MBPT) levels of approximation (38,39) for the total energy

$$E = E^{RHF\text{-}SCF} + E^{MBPT}, \qquad [3]$$

where the correlation energy is split into contributions that are due to different orders of MBPT

$$E^{MBPT} = E^{MBPT2} + E^{MBPT3} + E^{MBPT4} + \ldots, \qquad [4]$$

Through fourth-order in the correlation perturbation, the interaction energy in Eq. (2) was expressed in terms of the following components at any particular geometrical configuration **R**:

$$\mathbf{IE}^{Ground} = \mathbf{IE}^{SCF} + \mathbf{IE}^{MBPT2} + \mathbf{IE}^{MBPT3} + \mathbf{IE}^{MBPT4}. \qquad [5]$$

The necessary MBPT correlation energies were calculated using the BRATISLAVA package (40), interface to the MUNICH molecular package (41) for the Gaussian integrals, RHF-SCF eigenvectors and energies, molecular properties, and four-index molecular integral transformation calculations, respectively. In all calculations reported in the present work we have employed the medium-size polarized **POL1** basis sets of the CGTO type devised by Sadlej (42,43), which comprises (10.6.4/5.3.2) GTO/CGTO for C and O atoms, and (6.4/3.2) GTO/CGTO for hydrogen. This basis set accounts for the diffuseness of the valence part of the wave function, leads to a correct calculation of intermolecular electrostatic forces, and to a negligible secondary BSSE (44), which justifies the use of the standard counterpoise correction (22).

We have reported (45,46) the fourth-order MBPT counterpoise-corrected interaction energy of CO-H_2 in its ground electronic state, computed according to Eq. (2), using the **POL1** basis set for all possible configurations, having the CO or H_2 molecular bonds along the x, y, or z axis. On the supermolecule calculations, these two units were kept rigid at their experimental equilibrium bond lengths of 1.40a.u. and 2.132a.u. for H_2 and CO, respectively, so that only a rigid rotor potential surface resulted. The coordinate system used for the calculations is shown in Figure 1, where R represents the distance between the center of masses of CO and H_2, β_1 and β_2 are the polar angles of orientation of the vectors along the CO and H_2 bonds, and ϕ is the torsional angle. For each value of (β_1, β_2), geometry optimizations were carried out only with respect to the intermolecular parameter R, with the torsional angle fixed at ϕ=0. The full interaction energy surface depicted in Figure 2 shows that the linear **O-C···H-H** structure (IE(β_1 =0, β_2 =0), with the carbon atom closest to H) corresponds to the most stable conformation on these calculations, followed by the **C-O···H-H** colinear (IE(β_1 = 90, β_2 =0)), and the **parallel** (IE(β_1 =90, β_2 =90)), structure as the most stable conformations of CO-H_2.

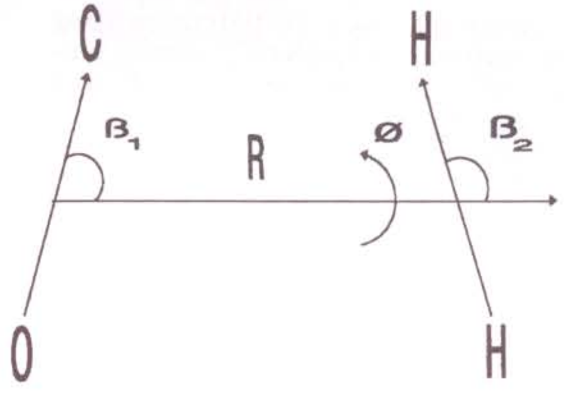

Figure 1. Coordinate System for CO-H_2.

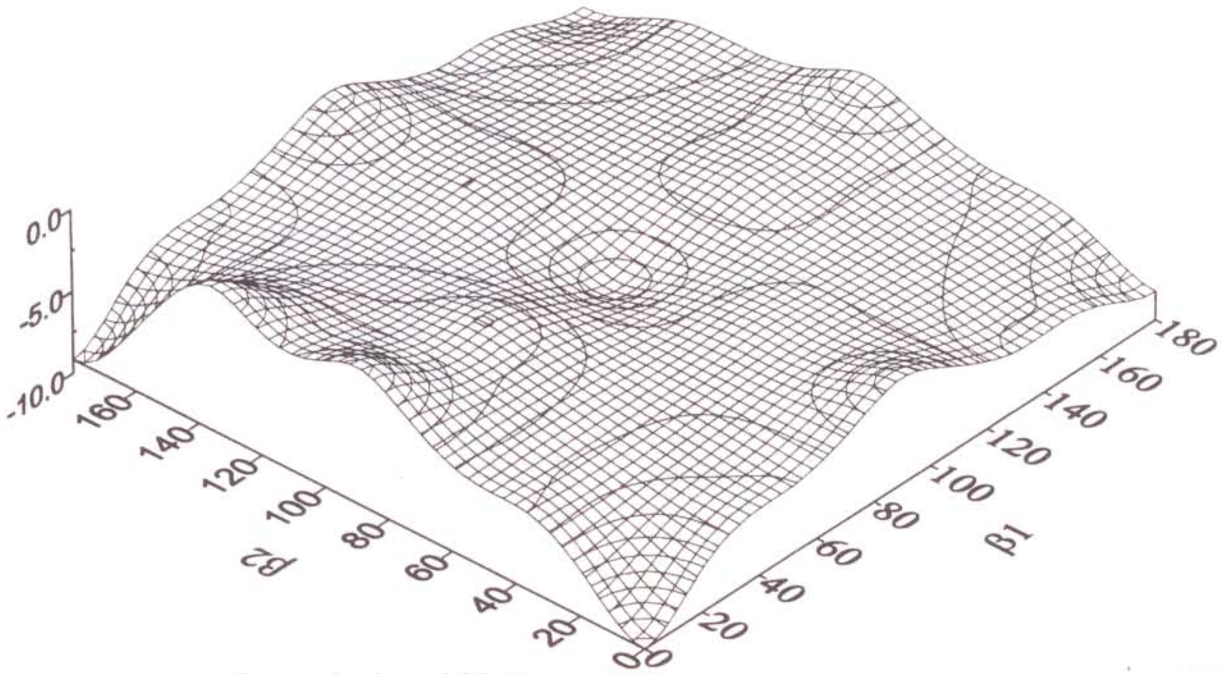

Figure 2. Interaction Energy Surface of CO-H_2.

Equilibrium bonding distances (R_e), the well depths (D_e), and dissociation energies (D_o), of the most stable **O-C···H-H** conformation, is obtained by fitting the above fully *ab initio* MBPT interaction-energy points for this conformer to a eight-order polynomial in the stretching coordinate R, analytically continued with a seventh-order polynomial on $1/R$ (from $1/R^6$ to $1/R^{12}$) in the asymptotic $R \to \infty$ region. The minimum of the interaction potential occurred (45,46) at R_e=8.1a.u. with a well depth of D_e=9.2meV. Vibrational energies were also calculated from fitted potential curves using the numerical renormalized Numerov procedure (47), by treating the linear **O-C···H-H** conformer as a diatomic system with only one degree of freedom R. The calculated dissociation energies corresponded to a D_o of 4.9meV with at least one vibrational state supported by this linear configuration, which agrees well with existing spectroscopic result (17,18).

Although all points on the calculated interaction energy curves are fully *ab initio*, the present results are to be taken only as a *qualitative guide*. In order to increase the predictive value of Figure 2, one is forced to improve the **POL1** basis to represent the dispersion energy more accurately, and to help represent the electric properties and correlation energy more accurately. Nevertheless, extending the size of the **POL1** basis is very difficult to accomplish in practice, mainly because the present correlation energy calculations are already extremely demanding on computational resources (CPU time and storage). Limited calculations performed with augmented basis sets (45,46) confirmed at least the relative energy order of the three lowest conformers found in the **POL1** basis sets, including close agreement within the reported values of R_e and D_o.

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