Franck–Condon Factors for Molecules Observed in Comets

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ABSTRACT: Franck-Condon Factors are calculated for the C_2^- and CO molecules and are used to identify these species in the optical spectra of comet C/2000WM1(LINEAR) and C/2000 C1 (Ikeya–Zhang). The present results compare well with those obtained by other methods. The optical spectra were recorded by means of the 2.12-m telescope at the Guillermo Haro observatory in Cananea, Sonora, México. © 2007 Wiley Periodicals, Inc. Int J Quantum Chem 107: 2650–2653, 2007

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Franck–Condon Factors (FCF) have become very useful quantities for the interpretation of molecular spectra, since they are directly related to the intensity of the observed lines. In the past, some works have been addressed to study those molecules that can be observed in comets or in the interstellar medium [1]. It is well known that comets are very rich in small molecules, in particular, diatomic and triatomic species [2]. Beside the FCF there are also other quantities, like r-centroids, which contribute to the line intensities, and have been considered recently by Reddy et al. [3], however, the role played by the FCF should be more important due to its dramatic variations through the different vibrational states.

Although extensive calculations have been performed [4] to study most of diatomic molecules, there still remain some of them (or some states of others) that have not been considered. Two examples of the latter are the subject of analysis in this study.

In this work, we will report some calculations carried out for the C_2^- and CO molecules tentatively detected in the comet C/2000 WM1(LINEAR) during November 2001 and comet Ikeya–Zhang on May 5, 2002 at the Guillermo Haro astrophysical observatory in México [5].

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TABLE I

Franck–Condon factors for $B^2\sum_u^+ - X^2\sum_g^+$ transitions of C_2^- calculated by: (i) Morse Potential with spectroscopic constants of ref. [10] and method of ref. [7] (uppermost entries). (ii) Morse Potential with spectroscopic constants of ref. [9] and Lefebvre-Brion software (middle entries). (iii) Jones et al. [10] (lowermost entries).

v/v'	0	1	2
0	0.7179	0.2494	0.0311
	0.717763	0.249538	0.031129
	0.7	0.3	0.03
1	0.2265	0.3268	0.3648
	0.226589	0.326571	0.364901
	0.2	0.3	0.4
2	0.0465	0.2943	0.1224
	0.046539	0.294305	0.122152
	0.05	0.3	0.1

FCF can be determined if the harmonic frequency w_e, the anharmonic frequency $w_e x_e$, the reduced mass μ, and the internuclear distance r_e of the potential energy curves of the diatomic molecules are known, in case of Morse potential. This involves the calculation of an overlap between vibrational wave functions [6]:

$$q_{mn} = |{}_G\langle m|n\rangle_E|^2$$

where G denotes the ground and E the excited states, respectively. Algebraic and numerical techniques have been devised to perform such calculations, the most accurate methods are either based on the Morse potential or on the RKR potential. For the Morse potential we have chosen a model based on a Simpson composite quadrature. This special numerical technique avoids overflows and underflows upon evaluation of the normalization constants and Laguerre polynomials. The numerical evaluation was done in the closed interval [0.4 Å, 2.5 Å] with a step size of $h = 0.01$ Å. Although there are many ways to calculate FCF using a Morse oscillator, a special software was written [7] following the technique of Halmann and Laulicht improving the numerical algorithms [8], and for the RKR we use a standard software [Lefebvre-Brion, H. private communication].

In Table I, we report the FCF for the first vibrational transitions corresponding to $C_2^- B^2\sum_u^+ - X^2\sum_g^+$ using the spectroscopic data of Mead et al. [9] obtained by ultrahigh resolution spectroscopy: $w_e = 1969.542(0.084)$ cm^{-1}, $w_e x_e = 15.100(0.057)$ cm^{-1}, $\mu = 6.0$, $r_e = 1.2234$ Å for $B^2\sum_u^+$ and $w_e = 1781.202(0.020)$ cm^{-1}, $w_e x_e = 11.6716(0.0048)$ cm^{-1}, $\mu = 6.0$, $r_e = 1.2684$ Å for the $X^2\sum_g^+$ electronic state. Our results yield a higher precision than those by Jones et al. [10], which were obtained with the RKR potential constructed from Dunham constants.

The present results can be used for detecting the presence of C_2^- in comets but also in atmospheres of cold carbon stars and in diffuse molecular clouds [11]. This molecule was observed for the first time in comets by Churyumov et al. from the emission spectrum of the Scorichenko–George comet [12]. It has also been searched in some other celestial objects like carbon stars [13] and was shown by quantum chemical calculations to have several stable excited states [14]. In the observed spectrum of C_2^- we found two emission lines, whose wavelengths are close to the theoretical wavelengths of the spectral lines of the transitions $B^2\sum_u^+ - X^2\sum_g^+$. This corresponds to observed wavelengths 4902.50 Å ($\lambda_{theor} = 4902.02$ Å, vibrational transition 1–0) and 5363.1 Å ($\lambda_{theor} = 5363.26$ Å, vibrational transition 1–1). The relative emission intensities (for 4902.02 Å is $I_{rel} = 0.26$ and for 5363.26 Å is $I_{rel} = 0.3$) are in good agreement with the Franck–Condon factor values for these transitions. As there are no other C_2^- transitions with high Franck–Condon factors in the comet spectrum (for example $\lambda_{theor} = 5415.87$ Å, vibrational transition 0–0, $\lambda_{theor} = 5912.69$ Å, vibrational transition 1–2, $\lambda_{theor} = 5987.82$ Å, vibrational transition 0–1), the C_2^- detection is rather preliminary.

In Tables II and III, we display the Franck–Condon Factors calculated with several methods for the Asundi ($a'^3\sum^+ - a^3\prod$) and triplet ($d^3\Delta - a^3\prod(2,1)$) bands of CO molecule. At a given vibrational level of the upper electronic state the FCF's have maxima

TABLE II

Franck–Condon factors for the Asundi band of CO observed in comet Ikeya–Zhang.

	Franck–Condon factors		
Transition	Morse	RKR	Kuzmenko
9–1	0.074042	0.075021	0.07477
10–2	0.068356	0.060706	0.06115
11–2	0.068336	0.065884	—
16–3	0.038048	0.043205	—
16–4	0.039829	0.039161	—
16–5	0.009277	0.006381	—

Spectroscopic constants were taken from reference [15] and potential curves from reference [16].

TABLE III

Franck–Condon factors for the triplet band ($d^3\Delta - a^3\prod(2,1)$) of CO observed in comet Ikeya–Zhang.

Transition	Franck–Condon factors		
	Morse	RKR	Kuzmenko
2–0	0.1163	0.114617	0.11508
3–0	0.1491	0.146591	0.14691
4–0	0.1552	0.152202	0.15259
5–0	0.1395	0.137533	0.13770
6–0	0.1126	0.111517	0.1140
8–1	0.0798	0.075184	0.07599
9–1	0.0825	0.079483	0.08000
12–2	0.0548	0.058120	0.05835
13–2	0.05732	0.059505	—

Spectroscopic constants were taken from reference [15] and potential curves from reference [16].

for 9–1, 10–2, 11–2, 16–4, 16–5 transitions of Asundi system and for 2–0, 3–0, 4–0, 5–0, 6–0, 8–1, 9–1, 12–2, 13–2 transitions of the triplet system. At a given vibrational level of the upper electronic state all transitions with maximal Franck–Condon factors values were observed in comet Ikeya–Zhang. It means that the relative intensities of the observed CO transitions correspond to its Franck–Condon factors values. There is only one exception for transitions from $a'^3\sum^+$, state with $v' = 16$. Franck–Condon factor is maximal for 16–3 transition but only 16–4, 16–5 transitions were detected.

From our observations it is possible to determine that the existence of CO optical bands leads mainly to formation of CO molecules at low vibrational states ($v' = 0-3$) of $a^3\prod$ state [17], estimated on the basis of the vibrational temperature (4,500 K) for $CO\ a^3\prod$ formed during CO_2^+ dissociative recombination and $(a' - a), (d - a), (e - a)$ cascade emission. This value corresponds to high relative population of only low vibrational levels ($v' = 0-3$). So, our results are in good agreement with the experimental data.

By knowing the relative intensities of electronic-vibrational transitions and their Franck–Condon factors, it is possible to determine relative populations of vibrational levels of the upper electronic state. In comet Ikeya–Zhang, the population of vibrational levels of CO molecules at $a'^3\sum^+$ and $d^3\Delta$ states is not under thermal equilibrium because vibrational levels with a large quantum number are highly populated. This is in agreement with experimental data [17]. In this work, the intensities of 6–0, 7–0, 8–0, 9–0 Asundi, 2–0, 3–0, 4–0 triplet transitions, and 2–0, 3–0 Herman transitions ($e^3\sum - a^3\prod$), were strong. At a given vibrational level of the upper electronic state intensities of electronic-vibrational transitions are proportional to their Franck–Condon factors. The comparison between intensities of observed transitions and their Franck–Condon factors shows good agreement. More accurate calculations that supports this relationship explicitly are in progress.

The first detection of CO bands in the optical spectrum of comet Bradfield 1980 t was conducted by Cosmovici et al. [18]. These authors considered dissociative recombination of CO_2^+ or HCO^+ as a possible mechanism for the origin of these bands. It was also noted that the reactions of dissociative recombination require high electron densities, a fluorescence mechanism can not explain the observed intensities of CO Asundi and triplet bands because the excitation rates are too low [19]. CO Asundi and triplet bands were observed in the following comets: Bradfield 1980 t in 1981, Scorichenko–George in 1991, WM1 (linear) in 2001 and 2002, and Ikeya–Zhang in 2002. These years correspond to periods of high solar activity. In all these comets, the bands were detected near the nucleus. It can be explained by formation of CO parent molecule in regions near the nucleus where high particle densities and high electron concentrations occur. Cosmovici et al. proposed that unusual events like an outburst can be a reason of CO Asundi and triplet band formation. During periods of high solar activity the flash and outburst activity of comets is increasing, this correlation supports Cosmovici et al.'s [18] hypothesis.

For explanation of CO Asundi and triplet bands intensities in comet Bradfield 1980 t about $3 \times 10^{30}-3 \times 10^{32}$ parent positive ions are required. During these calculations it was assumed that the rate coefficient of dissociative recombination is about $10^{-7}\,cm^3\,s^{-1}$ and the mean electron densities are $10^3-10^5\,cm^{-3}$. We can make this estimation more carefully because experimental results about CO_2^+ and HCO^+ are now available, and the rate constant of CO_2^+ recombination is about $3 \times 10^{-7}\,cm^3\,s^{-1}$ [20]. In the recombination of the CO_2^+ ground state with thermal electrons there is enough energy to populate $CO(a'^3\sum^+, v' < 11)$, $CO(d^3\Delta, v' < 6)$, and $CO(e^3\sum^-, v' < 3)$. The yields of CO molecules in these states during CO_2^+ recombination are 0.13, 0.081, and 0.017, respectively [13]. These experimental results are in agreement with our observations because Herman bands ($e^3\sum^- - a^3\prod$ transition) were much weaker than Asundi and triplet bands in comet Ikeya–Zhang. CO_2^+ recombination cannot explain

the origin of high excited vibrational levels of $a'^3\sum^+$ and $d^3\Delta$ states. HCO^+ must be refused as a parent *CO* molecule because HCO^+ recombination can produce only Asundi bands with $v' < 3$. The HCO^+ recombination is a more exoergic process and it can give rise to emissions from CO $(a', v' < 17)$, CO $(d, v' < 13)$, CO $(e, v' < 10)$. During HCO^+ recombination Asundi, triplet, and Herman bands were observed [17]. This parent molecule can explain all CO observed bands except the 16–3 triplet band. For formation of 15–3 triplet band, another parent molecule of high speed electrons is required. Although HCO^+ ion has been detected in comets [21], the concentration of this ion is too low, so, CO_2^+ is the best candidate for CO parent molecule. Formation of high excited vibrational levels of $a'^3\sum^+$ and $d^3\Delta$ states can be explained by CO_2^+ dissociative recombination with energetic electrons. The mean electron temperature in the pile-up region of comet Halley is $20,000°K$; such a value of electron temperature is enough for the formation of all observed CO bands in comet Ikeya–Zhang.

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